Contents

1 Periodic Classification of Elements and General Inorganic Chemistry

OVERVIEW

1. **Periodic table:** It classifies all the known elements in accordance with their properties in such a manner that elements with similar properties are grouped together in the same vertical column and elements with dissimilar properties are separated from one another.
2. **Dōbereiner's triads or law of triads:** Dōbereiner arranged similar elements in groups of three elements and showed that their atomic weights are either nearly the same or the atomic weight of the middle element is approximately the arithmetic mean of the other two. For example,

Triad:	Li	Na	K	Mean of first and third elements
At. wt.:	7	23	39	$\frac{7+39}{2} = 23$

The law of triads seemed to work only for a few elements. It was dismissed as coincidence.

3. **de Chancourtois classification or telluric screw (or helix) classification:** de Chancourtois arranged the then known elements in order of increasing atomic weights and made a cylindrical table of elements to display the periodic recurrence of properties.
4. **Newlands law of octaves:** Newlands arranged lighter elements in the increasing order of their atomic weights and noted that every eighth element had properties similar to the first element. This law seemed to be true only for elements up to calcium (Ca).
5. **Lothar Meyer classification:** Lothar Meyer plotted a graph between atomic volumes and atomic weights of the elements and observed that elements with similar properties occupied similar position on the curve.
6. **Mendeleev's periodic table:** It was based on atomic weights. The physical and chemical properties of elements are periodic functions of their atomic weights.

   Mendeleev proposed that some of the elements are still undiscovered and therefore left several gaps in the table. Both gallium (Ga) and germanium (Ge) were unknown at that time. He left the gap under aluminium (Al) and a gap under silicon (Si) and called these elements **EKa-aluminium and EKa-silicon.**

   Glenn T. Seaborg, the discoverer of element with atomic number 101, named this element as Mendelevium (Md) is his honour. Similarly, element 106 has been named Seaborgium (Sg) in Seaborg's honour.
7. **Modern periodic law:** The physical and chemical properties of the elements are periodic functions of their atomic numbers. This conclusion was obtained by Moseley's experiment. He observed regularities in the characteristic X-ray spectra of the element. Thus, a plot of $\sqrt{v}$ versus Z gave a straight line (where v is the frequency of X-rays emitted and Z is the atomic number).

   Modern periodic table arranges the elements in order of their atomic numbers in 7 horizontal rows (periods) and 18 vertical columns (groups or families). Atomic numbers in a period are consecutive, whereas in a group they increase in a pattern.

   Elements of the same group have similar **valence shell** electronic configuration and, therefore, exhibit similar chemical properties. However, elements of the same period have incrementally increasing number of electrons from left to right and, therefore, have different valencies.
8. **IUPAC nomenclature of elements with $Z > 100$:** Both the American and Soviet scientists claimed credit for discovering element 104. The Americans named it Rutherfordium (Rf) whereas the Soviets named it Kurchatovium. To avoid such problems, the IUPAC has made recommendation that until a new element's discovery is proved and its name is officially recognised, a systematic nomenclature be derived directly from the atomic number of the element using the numerical root for 0 and numbers 1–9. The roots are put together in order of digits which make up the atomic number and 'ium' is added at the end.

   For example, IUPAC name and symbol for the element with atomic number 121 is unbiunium (Ubu).

   As of now, elements with atomic numbers up to 112, 114 and 116 have been discovered. Elements with atomic numbers 113, 115, 117 and 118 are not yet known.
9. **Classification of elements:** Four types of elements can be recognised in the periodic table on the basis of their

electronic configurations. These are *s*-block, *p*-block, ***d*-block, and *f*-block elements.**

Hydrogen with one electron in the 1*s* orbital occupies a unique position in the periodic table.

10. ***s*-Block elements:** The elements of groups 1 and 2, including hydrogen and helium, in which the *s*-orbitals are being progressively filled in are called *s*-block elements. The total number of elements in *s*-block are 14.

    General outer shell electronic configuration of *s*-block elements is ns^{1-2}, where n is 2–7.

11. ***p*-Block elements:** The elements of groups 13 to 18 (excluding helium) in which *p*-orbitals are being progressively filled in are called ***p*-block elements.** The total number of elements in *p*-block are 30 in the periodic table.

    General outer shell electronic configuration of *p*-block elements is $ns^2\ np^{1-6}$, where n is 2–6.

12. ***d*-Block elements:** Elements in which the last electron (differentiating electron) enters into penultimate shell, i.e., $(n-1)d$ orbitals are called ***d*-block elements.**

    General outer shell electronic configuration of *d*-block elements is $(n-1)d^{1-10}\ ns^{0-2}$, where n is 4–7.

13. ***f*-Block elements:** Elements in which the last electron (differentiating electron) enters into the antepenultimate shell, i.e. $(n-2)f$ orbitals are called ***f*-block elements.**

    General outer shell electronic configuration of f-block elements is $(n-2)f^{0-14}\ (n-1)d^{0-1}\ ns^2$, where n is 6–7.

14. **Metals, non-metals and metalloids**

    a. **Metals:** They comprise 78% of all the known elements. They are usually solid at room temperature with high melting and boiling points. But mercury (Hg) is liquid at room temperature. However, Ga (303 K), Cs (302 K) and Fr (300 K) have low melting points.

    They are good conductor of heat and electricity, malleable and ductile.

    Ga (gallium), a liquid metal, is used in making high-temperature thermometer. Similarly, Ge (germanium), a liquid metal, is transparent in the infrared (IR) region and, therefore, is used in the making of infrared windows, prisms and lenses.

    b. **Non-metals:** They are located at the top right-hand side of the periodic table and are less than 20 in number (i.e. 18). They are either solid or gas (except bromine which is a liquid) at room temperature with low melting and boiling points, poor conductor of heat and electricity, brittle, neither malleable nor ductile.

    Boron and carbon have high melting and boiling points.

    c. **Metalloids or semi-metals:** Elements which lie at th border line between metals and non-metals (e.g., Si, G As, Sb and Te) are called **metalloids or semi-metals.**

    d. **Trends in metallic and non-metallic character** Metallic character increases down the group (↓) wherea decreases from left to right in a period (→). The tren is reverse for non-metallic character. The physical an chemical properties of elements vary periodically wit their atomic number.

    e. **The useful mnemonic of remembering the metalli character series**

Decreasing order of metallic character is given below:

K > Na > Ba > Ca > Mg > Al > Zn > Fe > Ni > Sn > P $\boxed{H}$ > Cu > Hg > Ag > Au > Pt

The useful mnemonic to remember the metallic series is:

$\boxed{\text{PSBC}}$ $\boxed{\text{MAZINTL}}$ H $\boxed{\text{CHAAP}}$

PSBC	MAZINTL	CHAAP
P = Potassium (K)	M = Magnesium (Mg)	C = Copper (Cu)
S = Sodium (Na)	A = Aluminium (Al)	H = Mercury (Hg)
B = Barium (Ba)	Z = Zinc (Zn)	A = Silver (Ag)
C = Calcium (Ca)	I = Iron (Fe)	A = Gold (Au)
	N = Nickel (Ni)	P = Platinum (Pt)
	T = Tin (Sn)	
	L = Lead (Pb)	

↓

$\boxed{\text{Non-metal}}$

Note: That hydrogen is not a metal and comes betwee MAZINTL and CHAAP

15. **Advantages and defects of the modern or long form the periodic table**

    a. **Advantages:**

    i. It correlates the position of elements to the electron configuration of their atoms, and thus, elements hav been grouped into *s*-, *p*-, *d*- and *f*-blocks. This h helped to understand their properties more easily.

    ii. The transition elements of 3*d*, 4*d*, 5*d* and 6*d* a assigned proper positions in this periodic table.

    iii. Elements of groups 8–10 consisting of nine elemen in three triads (group VIII of the Mendeleev periodic table) are assigned proper positions in th periodic table.

    b. **Defects:**

    i. Although hydrogen has been placed along wi alkali metals in group 1 and halogens in group 1 yet its position is not settled. Hydrogen shows ma properties similar to both group 1 and 17 element

    ii. Lanthanides and actinides have not been include in the main part of the periodic table.

16. **Periodic properties:** The properties which are related electronic configuration and which show a regular gradatio

down the group (↓) and along the period (→) are called periodic properties.

17. **Atomic radius:** Considering an atom to be spherical, the atomic size is the radius of the sphere and known as atomic radius.

It is defined as the distance from the centre of the nucleus to the outermost shell containing electrons.

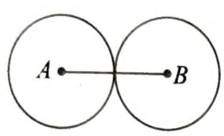
OR

The distance from the centre of the nucleus to the point up to which the density of electron cloud (i.e., probability of finding the electron) is maximum.

Depending upon whether an element is a metal or a non-metal, there are four different types of atomic radii:

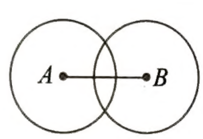
a. **Metallic radius:** It is half the internuclear distance separating the metal cores in the metallic crystal.

$\therefore r = \frac{1}{2} AB$



(No overlapping of atomic orbitals)

b. **Covalent radius:** It is one-half of the distance between the nuclei of two covalently bonded atoms of the same element in a molecule.



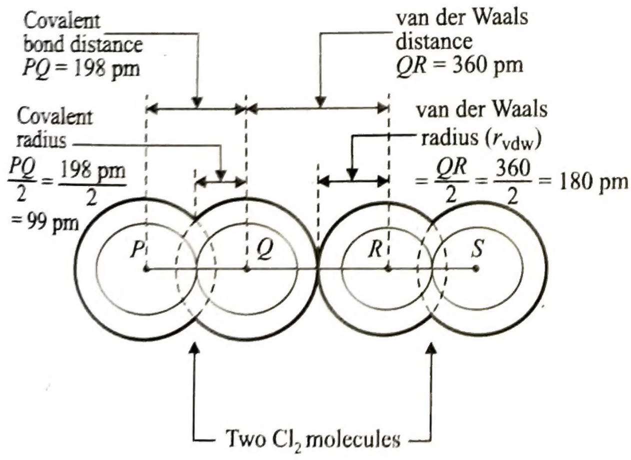
$\therefore r = \frac{1}{2} AB$

(Overlapping of atomic orbitals to form a covalent bond)

∴ Metallic radius > Covalent radius

c. **van der Waals radius:** It is one-half of the distance between the nuclei of two identical non-bonded isolated atoms. Thus,

van der Waals radius > Metallic radius > Covalent radius.



(Comparison of van der Waals and covalent radii in two Cl_2 molecules)

van der Waals radii (r_{vdw}) ∝ Number of energy shells

and

$$r_{vdw} \propto \frac{1}{\text{Nuclear charge}}$$

Thus, r_{vdw} of Br > r_{vdw} of Cl > r_{vdw} of F.

Similarly,

r_{vdw} of N > r_{vdw} of O > r_{vdw} of F,

and r_{vdw} of P > r_{vdw} of S.

d. **Ionic radii:** Ionic radii in an ionic crystal is calculated from the internuclear distance between the two ions (i.e. cation and anion).

i. **Radius of cation:** It is smaller than that of the corresponding neutral atom.

ii. **Radius of anion:** It is larger than that of the corresponding neutral atom.

18. **Variation of atomic and ionic radii in the periodic table:** Generally, the covalent or van der Waals radii increases down the group (↓) and decreases along the period (→).

Both cationic and anionic radii increase down the group (↓) due to increase in the number of shells.

Exceptions: Elements of 2nd and 3rd transition series belonging to same vertical columns are similar in size and properties because of the intervention of lanthanides.

19. **Isoelectronic species:** They are ions of different elements having same number of electrons but different nuclear charge (Z).

Ionic radii of isoelectronic species decrease with the increase in the magnitude of nuclear charge (Z), e.g. ionic radii, decreases in the order (all have 10 electrons but with $Z = +7, +8, +9, +11, +12$ and $+13$) as:

$N^{3-} > O^{2-} > F^{\ominus} > Na^{\oplus} > Mg^{2+} > Al^{3+}$.

20. **Ionisation enthalpy (IE):** It is the minimum amount of energy required to remove the outermost shell electron from an isolated gaseous atom to form a gaseous ion (represented as IE or $\Delta_i H^{\ominus}$).

It is measured in eV atom^{-1} or kcal mol^{-1} or kJ mol^{-1}.

1 eV atom^{-1} = 23.06 kcal mol^{-1} = 96.49 kJ mol^{-1}

21. **Successive ionisation enthalpies:** The ionisation enthalpies to remove first, second, and third electrons, etc., from an isolated gaseous atom are called successive ionisation enthalpies.

$IE_3 > IE_2 > IE_1 >$ or $\Delta_i H_3^{\ominus} > \Delta_i H_2^{\ominus} > \Delta_i H_1^{\ominus}$

22. **Factors affecting the magnitude of ionisation enthalpies**

a. Size of an atom

b. Z_{eff} (effective nuclear charge)

c. Screening effect

d. Penetration effect

e. Electronic configuration

23. **Variation of IE in the periodic table:** IE_1 generally decreases down the group (↓) and increases along the period (→).

Exception:

a. IE_1 of Be > IE_1 of B

IE_1 of Mg > IE_1 of Al
IE_1 of N > IE_1 of O
IE_1 of P > IE_1 of S

b. Exception of IE in group 13 elements.

Elements:	B >	Al <	Ga >	In <	Tl
IE_1(kJ mol^{-1}):	801	577	579	558	589

Exception in IE_1: Ga > Al (imperfect shielding of $3d$ orbitals in Ga).

c. General trend in IE_1 from $3d \rightarrow 4d$ series is observed but not in $4d \rightarrow 5d$ series because of the incorporation of the 14 lanthanide elements between La and Hf. $5d$ series have the highest IE_1. The increase in radius due to the addition of extra shell is compensated by the decrease in radius due to lanthanide contraction.

Hence, the radii of $4d$ and $5d$ elements more or less remain the same, due to which Z_{eff} increases to more extent, which results in high IE_1 of the $5d$ elements of transition series.

24. Electron gain enthalpy ($\Delta_{eg}H^{\ominus}$): It is the energy released when a neutral isolated gaseous atom accepts an extra electron to form the gaseous ion, i.e., anion.

$\Delta_{eg}H^{\ominus}$ for halogens (group 17) is highly negative, because they attain stable noble gas configuration by accepting an extra electron. Whereas noble gases have large positive $\Delta_{eg}H^{\ominus}$ value because the extra electron has to be added in the next higher principal quantum energy level thereby producing highly unstable electronic configuration.

Like ionisation energy, $\Delta_{eg}H^{\ominus}$ is measured either in eV atom^{-1} or kJ mol^{-1} or kcal mol^{-1}.

25. Successive electron gain enthalpies: The energy released to add first, second, third electrons and so on to an isolated gaseous atom is called successive electron gain enthalpy.

The addition of second electron is opposed by the electrostatic repulsion and hence energy is required for the addition of second electron. Thus, the second electron gain enthalpy of an element is positive.

For example, $\Delta_{eg}H_1^{\ominus}$ of oxygen $= -141$ kJ mol^{-1}
but $\Delta_{eg}H_2^{\ominus}$ of $O^{\ominus} = +780$ kJ mol^{-1}

26. Variation of $\Delta_{eg}H^{\ominus}$ in the periodic table: Generally $\Delta_{eg}H_1^{\ominus}$ decreases (less negative) down the group (↓) but increases (more negative) along the period (→).

27. Factors affecting the magnitude of $\Delta_{eg}H^{\ominus}$

a. Size of an atom
b. Z_{eff} (Effective nuclear charge)
c. Electronic configuration

Some exceptions:

i. $\Delta_{eg}H_1^{\ominus}$ of Cl > F > Br > I
ii. $\Delta_{eg}H_1^{\ominus}$ of Al > B
iii. $\Delta_{eg}H_1^{\ominus}$ of P > N
iv. $\Delta_{eg}H_1^{\ominus}$ of S > O

28. Electronegativity (EN): It is the tendency of an atom to attract shared pair of electrons towards itself in a covalently bonded molecule. It is represented as χ (chi) or EN.

It is not a measurable quantity. However, various numerical scales of EN have been developed.

The EN of any element is not constant and varies depending upon the element to which it is bonded.

29. Variation of EN in the periodic table: Generally, it increases along the period (→) and decreases down the group (↓).

F is the most EN element with a value of 4.0 and C is the least EN element.

Exceptions:

a. EN of Ga and Ge > EN of Al and Si
(due to the d-block contraction)

b. EN of Pb > EN of Tl and Bi

30. Factors affecting the magnitude of EN:

a. Atomic radius $\left(EN \propto \frac{1}{\text{Atomic radius}}\right)$

b. Z_{eff} (Effective nuclear charge) (EN $\propto Z_{eff}$)

c. Number of inner shells

$$\left(EN \propto \frac{1}{\text{Number of inner shells}}\right)$$

d. Charge on the ion or oxidation state of the atom
(EN $\propto$ Number of positive charge)

$$\left(EN \propto \frac{1}{\text{Number of negative charge}}\right)$$

e. Nature and number of substituent atoms attached to the atom

f. State of hybridisation (EN $\propto$ s-character in the hybrid orbital)

EN decreases from $sp > sp^2 > sp^3$ hybrid orbital.

g. IE and $\Delta_{eg}H^{\ominus}$: (EN $\propto$ Higher IE or higher or more negative $\Delta_{eg}H^{\ominus}$)

h. EN $\propto$ non-metallic character of elements

i. $\left(EN \propto \frac{1}{\text{Metallic character of elements}}\right)$

Thus, along the period (→) non-metallic character increases and down the group (↓) metallic character increases.

31. Scales of EN

a. Pauling scale:

$$(\chi_A - \chi_B) = 0.208\left[E_{A-B} - \sqrt{(E_{A-A} \times E_{B-B})}\right]^{\frac{1}{2}}$$

kcal mol^{-1}

where χ_A and χ_B are the EN's of two atoms A and B and E_{A-B}, E_{A-A} and E_{B-B} are bond energies of molecules A – B, A_2 and B_2, respectively, in kcal mol^{-1}.

In SI units,

$(\chi_A - \chi_B) = 0.1017\sqrt{\Delta_{A-B}}$, where Δ is in kJ mol^{-1}

and $\Delta_{A-B} = \left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}\right]$

Another form of the equation can be written as:

$$(\chi_A - \chi_B) = (eV)^{-1/2}\sqrt{E_{A-B} - \frac{1}{2}[E_{A-A} + E_{B-B}]}$$

$$= 0.208\sqrt{E_{A-B} - \frac{1}{2}[E_{A-A} + E_{B-B}]}\ (\text{kcal mol}^{-1})$$

$$= 0.1017\sqrt{E_{A-B} - \frac{1}{2}[E_{A-A} + E_{B-B}]}\ (\text{kJ mol}^{-1})$$

b. Mulliken's scale:

i. EN or $\chi_A = \left[\frac{(IP)_A + (EA)_A}{2}\right]$, where IP = Ionisation potential and EA = Electron affinity in eV.

ii. If IP and EA are in kcal mol^{-1}, then

$$EN(\text{or } \chi_A) = \frac{(IP)_A + (EA)_A}{2 \times 62.5}$$

iii. If IP and EA are in kJ mol^{-1}, then

$$EN(\text{or } \chi_A) = \frac{(IP)_A + (EA)_A}{540}$$

iv. Mulliken's values of EN are about 2.8 times more than the Pauling scale, i.e.,

EN Pauling (or χ Pauling) = χ Mulliken/2.8.

$$= \frac{(IP)_A + (EA)_A}{2 \times 2.8}$$

The constant $\frac{1}{2 \times 2.8} = \frac{1}{5.6}$ is called scale adjustment factor. This factor is used when IP and EA are in eV.

v. Pauling scale in terms of $\Delta_{eg}H^{\ominus}$:

$\chi_{Pauling} = [IE - \Delta_{eg}H^{\ominus}]/2$

The Mulliken EN values are scaled down to match the Pauling value by dividing $\left(\frac{IP + EA}{2}\right)$ in eV by 3.17.

c. Allred–Rochow's scale:

$$EN(\text{or } \chi_A) = 0.359 \times \frac{Z_{eff}}{r^2} + 0.744$$

where r is the radius of an atom in A°. The value of Z_{eff} is calculated from Slater's rule taking all the electrons.

32. Non-polar and polar bonds:

a. A bond between two similar atoms is non-polar.

b. If the EN's of the two atoms forming a bond are different and the bonded atoms acquire $a + \delta$ and $-\delta$ charges is called a polar covalent bond.

c. Higher the difference in EN of two bonded atoms, the molecule is more polar and have higher dipole moment (μ).

i. When $(\chi_A - \chi_B) = 1.7$, the bond is 50% ionic and 50% covalent.

ii. When $(\chi_A - \chi_B) < 1.7$, the covalent character is more than 50%.

iii. When $(\chi_A - \chi_B) > 1.7$, the ionic character is more than 50%.

d. Percentage of ionic character:

% of ionic character = $[16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2]$

when $(\chi_A - \chi_B) = 2.1$, the compound is 50% ionic

e. $(\chi_A - \chi_B) \propto$ bond strength

33. Acidic and basic nature of oxides of normal elements : The acidic nature of oxides of normal elements increases whereas the basic nature decreases along the period ($\rightarrow$) due to increase of EN from left to right in a period.

34. Bond length:

a. Generally, in case of heteroatomic molecule of AB type, bond length (d_{A-B}) is equal to the sum of covalent radii of A and B atoms.

$$d_{A-B} = \chi_A + \chi_B$$

b. $d_{A-B} \propto \frac{1}{\%\text{ of ionic character}}$

c. $d_{A-B} \propto \frac{1}{(\chi_A - \chi_B)} \propto$ stability of AB molecule

35. Bond angle: For AB_x-type molecule (where A is the central atom, B is the atom attached with atom A and x is the number of B atoms), then B–A–B bond angle changes as given.

a. If the EN of central atom decreases and/or the size increases the bond angle decreases, i.e. the bond angle decreases down the group, e.g. bond angle of $NH_3 > PH_3 > AsH_3 > SbH_3$ and $H_2O > H_2S > H_2Se > H_2Te$.

b. If the EN of atom B decreases, the bond angle (B–A–B) increases, e.g. bond angle of $PI_3 > PBr_3 > PCl_3$ and $NH_3 > NF_3$ and $OH_2 > OF_2$.

c. Molecules or ions without nonbonding electrons (i.e. lone pair of e^-'s) on central atom and having regular geometry, the change in the EN of central atom or surrounding atom has no effect on the bond angle. For example, bond angle of $BF_3 = BCl_3 = BBr_3 = AlCl_3 = 120°$ and similarly $CH_4 = CBr_4 = CCl_4 = \overset{\oplus}{N}H_4 = 109°28'$.

d. For the molecule with same central atom with vacant d-orbitals and with different B atom, bond angle increases with the increase of EN of B atom having lone pair of elctrons. For example, bond angle of $PF_3 > PH_3$ (opposite to NH_3 and NF_3) (i.e., opposite of point (b)).

e. Bond angle of $sp > sp^2 > sp^3$ hybrid orbitals (180° > 120° > 109°28′) For example,

Bond angle of $NO_2^{\oplus} > NO_2 > NO_3^{-} > NO_2$

Bond angle: 180° > 134° > 120° > 115°

36. Variation of valence in the periodic table: Along the period (→), the number of valence electrons increases from 1 to 8. But the valence of element w.r.t. H or O, first increases from 1 to 4 and then decreases to zero.

Down the group (↓) elements exhibit same valence.

37. Typical elements: They are elements of 3rd period. These include Na, Mg, Al, Si, P, S and Cl. The properties of all elements belonging to a particular group resemble the properties of the corresponding typical elements of that group. For example, the general properties of group 1 can be predicted from the behavior of Na not Li, the first member of the family.

38. Bridge elements: They are elements of 2nd period and their properties resemble the properties of elements of 3rd period placed diagonally as shown:

$$\begin{array}{l|llll} \text{2nd period} & \text{Li} & \text{Be} & \text{B} & \text{C} \\ \text{3rd period} & \text{Na} & \text{Mg} & \text{Al} & \text{Si} \end{array}$$

This anomalous behaviour is due to the

a. Small size

b. High charge density

c. High polarising power

d. High EN of the element

39. Periodic trends and chemical reactivity:

a. Chemical reactivity of an element is shown by its reactions with oxygen and halogens.

b. The normal oxide formed by the elements on extreme left is the **most basic** (e.g. Cs_2O), whereas that formed by the element on extreme right is the **most acidic** (e.g. OF_2 and Cl_2O_7).

c. Oxides of elements in the centre are **amphoteric** (e.g. Al_2O_3, As_2O_3) or **neutral** (e.g. CO, NO, N_2O).

40. Magnetic properties:

a. Diamagnetic substances are weakly repelled by the applied magnetic field and have all the electrons paired in their atoms, e.g. NaCl and H_2O.

b. Paramagnetic substances are attracted by the applied magnetic field and has one or more unpaired electrons in their atom, e.g., Fe^{3+} and Cr^{3+}.

c. Ferromagnetic substances keep their magnetism even after the magnetic field is removed, e.g., Fe, Co and Ni.

Using 'spin only' formula, the magnetic moment is given as

$$\mu_s = \sqrt{n(n+2)}\ \text{BM}$$

where n is the number of unpaired electrons and it is measured in Bohr Magneton (BM).

$$1\,\text{BM} = \frac{eh}{4\pi mc} = 9.27\times10^{-21}\ \text{ergs gauss}^{-1}$$

OR

$$\left.\begin{array}{c} = 9.27\times10^{-24}\ \text{J Tesla} \\ \text{OR} \\ = 9.27\times10^{-24}\ \text{Am}^2 \end{array}\right] \text{(SI units)}$$

41. Fajans' rule: It tells about the covalent character or polarisability of a compound. The compound is more covalent when it has the following conditions:

a. Higher charge on the ions (cation or anion)

b. Small cation

c. Large anion

d. Presence of d electrons

42. Inert pair effect: In groups 13–16, down the group (↓), the stability of lower oxidation state increases. This is due to ineffective shielding of ns^2 electrons of valence shell by the intervening d- and f-electrons. So, ns^2 electrons do not participate in bond formation and behave as inert pair. For example, in group 13 Tl exists as $Tl^{\oplus}$, in group 14, Pb exists as Pb^{2+}, and in group 15 Bi exists as Bi^{3+}, oxidation states.

43. Factors that determine the stability of compounds: The stability of a compound is due to the following conditions:

a. The compound must have high EN of the element to excite electrons from central atom to vacant orbitals

b. The central atom must have vacant orbitals

c. Inert pair effect

d. Appropriate sizes of cations and anions, for example,

i. NH_3 and NCl_3 exist, but NH_5 and NCl_5 do not exist.

ii. PCl_5 exists, but PBr_5 and PI_5 do not exist.

iii. PH_3 exists, but PH_5 does not exist.

iv. TlCl, $PbCl_2$ and $BiCl_3$ are more stable than $TlCl_3$, $PbCl_4$ and $BiCl_5$.

v. IF_7 exists, but ICl_7 does not exist.

vi. $AlCl_3$ exists as dimer (Al_2Cl_6), but BCl_3 does not exist.

44. Lattice enthalpy ($\Delta_U H^{\ominus}$): It is the amount of energy released when crystal lattice of one mole of solid ionic compound is formed from their gaseous constituent ions. For example,

$Na^{\oplus}_{(g)} + Cl^{\ominus}_{(g)} \rightarrow NaCl_{(s)}$, $\Delta_U H^{\ominus} = -788\ \text{kJ mol}^{-1}$

It depends on the following factors:

a. Size of the ions

b. Magnitude of charges on the ions

Thus, $\Delta_U H^{\ominus} \propto \dfrac{|Z^{\oplus}|Z^{\ominus}|}{r_0}$, where $|Z^{\oplus}|\,|Z^{\ominus}|$ are charges of cation and anion respectively and r_0 is the interionic distance.

Down the groups (↓) generally, it decreases and increases along the period (→).

It is determined by the use of Born–Haber cycle, which is based upon Hess's law of heat summation.

Application of lattice energy: It explains the formation of oxides, peroxides and superoxides of group 1 and group 2 elements.

45. a. **Hydration energy:** It is the amount of energy released when one mole of gaseous ions is dissolved in excess of water to give its constituent aqueous ions, e.g.,

$Na^{\oplus}(g) + Cl^{\ominus}(g) + aq \rightarrow Na^{\oplus}(aq) + Cl^{\ominus}(aq)$

$$\Delta_{hyd}H^{\ominus} = -ve$$

b. **Trend in the periodic table:** Generally, hydration energy decreases down the group (↓) and increases along the period (→).

$$\Delta_{hyd}H^{\ominus} \propto \text{charge density}\left(\text{i.e. } \frac{\text{charge}}{\text{size}} \text{ ratio}\right)$$

c. **Application:**

i. Solubility is water:

If $\Delta_{hyd}H^{\ominus} > \Delta_U H^{\ominus}$, the compound is soluble in water.
If $\Delta_{hyd}H^{\ominus} < \Delta_U H^{\ominus}$, the compound is not soluble in water.

ii. Lithium is the strongest reducing agent in aqueous solution.

iii. Ionic mobilities in electric fied of *s*-block ions.
Order of decreasing mobilities:
$Cs^{\oplus} > Rb^{\oplus} > K^{\oplus} > Na^{\oplus} > Li^{\oplus}$
$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Be^{2+}$

iv. Ionic radii in aqueous solution of ions of *s*-block elements.
Order of decreasing radii of hydrated ions:
$Li^{\oplus} > Na^{\oplus} > K^{\oplus} > Rb^{\oplus} > Cs^{\oplus}$
$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

v. Compounds of group 2 elements exist as hydrated salts, e.g. $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6\,H_2O$, whereas NaCl and KCl do not form such hydrates but LiCl exists as $LiCl \cdot 2H_2O$.

vi. Lanthanides and actinides show, in general, +3 oxidation state.

vii. $Cu^{\oplus}$ compounds are unstable in equeous solution and undergo disproportionation.
$2\,Cu^{\oplus} \rightarrow 2Cu^{2+} + Cu$

viii. Solubilities in water of hydroxides and fluorides of group 2 elements increase down the group (↓). For example, increasing order of solubilities is as follows:
$BeF_2 < MgF_2 < CaF_2 < SrF_2 < BaF_2$.
$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

ix. Solubilities in water of carbonates, bicarbonates and sulphates of group 2 elements decreases down the group (↓). For example, the decreasing order of solubility is as follows:
$BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$
$Be(HCO_3)_2 > Mg(HCO_3)_2 > Ca(HCO_3)_2 > Sr(HCO_3)_2 > Ba(HCO_3)_2$
$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

46. **Flame colouration:** When the elements or their salts are heated in a bunsen flame, they impart characteristic colour to the flame.

Principle: Same excitation energy of bunsen flame excites electrons in different element to different level due to difference in their IE's.

Flame colouration	Li	Na	K	Rb	Cs	
Group 1	Crimson	Golden yellow	violet	Red violet	Blue	
Group 2	Be	Mg	Ca	Sr	Ba	Ra
	–	–	Brick red	Crimson	Apple green	Crimson
Cu	Deep bluish green					
Pb	Pale blue grey					

Be and Mg do not impart flame colourations, since the excitation energy of the flame is not sufficient to excite electrons to higher energy level, due to very high IE of Be and Mg.

47. **Colour of substance in visible light:** When molecules absorb light of specific wavelengths in the visible region of electromagnetic spectrum, the outer (valence) electrons are excited to higher energy levels. When these excited electrons return to their original (ground) energy level, they emit radiation in the visible region corresponding to the energy absorbed and give complementary colours.

Application:

a. Halogens are coloured, e.g.

Halogens	Observed (complimentary colour)
F_2 (g)	Yellow
Cl_2 (g)	Greenish yellow
Br_2 (l)	Red or brown or orange
I_2 (s)	Violet

b. When group 1 elements are dissolved in liquid NH_3, they give blue colour whereas group 2 elements give deep blue black colour.

c. **The colour in the coordination compounds:**

i. It is explained in terms of CFT (crystal field theory). It is due to *d–d* transition or more specifically $(t_{2g} \rightarrow e_g)$ transition in case of octahedral complexes and $(e \rightarrow t_2)$ transition in case of tetrahedral complexes.

ii. The colour in lanthanides and actinides is due to *f–f* transitions.

iii. Colour of compounds having d^0 configuration i.e., when *d*-orbitals are empty, colour is due to charge transfer theory, e.g., purple colour of $KMnO_4$ and orange colour of $K_2Cr_2O_7$.

iv. Some solid compounds change their colour on heating due to non-stoichiometric defects, i.e., metal excess defects and these are of two types (i) Anion vacancies or F-centre and (ii) the presence of extra cations in interstitial sites.

For example, when alkali metal halides are heated in alkali metal vapours, the colour is observed (due to

F-centre). Excess of Li in LiCl gives a pink colour and excess of K in KCl makes it violet.

On heating ZnO turns yellow and on cooling it turns white due to the presence of extra cations in interstitial sites.

48. ***pπ–pπ* bond:** C, N and O have unique ability to form *pπ–pπ* multiple bond with itself and with other elements having (i) small size (ii) high EN, (iii) high IE and (iv) non-availability of *d*-orbitals.

49. **(*pπ–dπ*) multiple bonding:** Heavier members of groups 14, 15 and 16 form *pπ–dπ* bonds by the overlap of *p*-orbital of one atom and *d*-orbital of another atom. This tendency is found particularly in case of Si linked to O and N.

Examples:

a. Trimethyl amine, $N(CH_3)_3$, is pyramidal and more basic whereas trisilyl amine, $N(SiH_3)_3$, is planar and is less basic.

b. CCl_4 and $SiCl_4$, both are covalent compounds, but CCl_4 is not hydrolysed with water while $SiCl_4$ is hydrolysed (due to *pπ–dπ* multiple bonding).

c. MnF_7 does not exist, although Mn_2O_7 exists, due to the ability of oxygen to form *pπ–dπ* multiple bonds.

50. Summary of trends of periodic properties:

a. Increases along the period

Decreases down the groups

The following properties decrease down the group (↓) but increase along the period (→).

1. IE, EA, $\Delta_{eg}H^\ominus$ and EN.
2. Lattice enthalpy $(\Delta_U H^\ominus)$, hydration enthalpy $(\Delta_{hyd}H^\ominus)$
3. Charge density $\left(\dfrac{\text{charge}}{\text{size}}\text{ ratio}\right)$
4. Metallic bonding
5. Non-metallic character
6. Acidic character of oxides

b. The following properties increase down the group (↓) and decrease along the period (→)

Increases down the group (↓)

Decreases along the period

1. Atomic radii
2. Metallic character
3. Basic character of oxides
4. Electropositivity or metallic character

51. Some important facts:

- Metals have low IE and low EN whereas non-metals have high IE and high EN.
- I_2 sublimes on heating and is a non-metal with metallic lusture.
- Br_2 is a liquid non-metal at room temperature.
- Hg is the lowest melting point liquid metal.
- Gallium (Ga) (m. pt. 29.8°C), caesium (Cs) (m. pt. 28.5°C) and francium (Fr) (m. pt. 27.0°C) are metals having low melting points.

  Ga is used in making high temperature thermometer because of its low melting and high boiling points.
- Germanium (Ge) is transparent in the infrared (IR) region and therefore it is used in the making of infrared windows, prisms and lenses.
- Selenium (Se) is used as a photo conductor in photo copying (Xerox) machines and also for decolouriser of glass.
- Tellurium (Te) and polonium (Po) are highly toxic, the latter more so because of intense radioactivity.
- Among metals, tungsten (W) has highest melting and boiling points.
- Na, K, Rb and Cs are kept in kerosene oil.
- Phosphorous (P_4) (white or yellow) is kept in water.
- Fluorine (F) is the most EN element and caesium (Cs) is the most EP (electropositive) element.
- $H^\ominus$ and $I^\ominus$ ions are the smallest and largest anions, respectively.
- $H^\oplus$ and $Cs^\oplus$ are the smallest and largest cations, respectively.
- Helium (He) has the maximum ionisation potential.
- Oxygen is the most abundant element on the earth.
- Aluminium (Al) is the most abundant metal.
- Iron (Fe) is the most abundant transition metal.
- Nitrogen (N_2) is the most abundant gas in atmosphere.
- Among metals silver (Ag) is the best conductor of electricity and lead (Pb) is the poorest conductor of electricity.
- Among non-metals, carbon (C) has the highest melting point (4100°C).
- Diamond (carbon) is the hardest natural substance.
- Chlorine (Cl) has maximum EA or $\Delta_{eg}H^\ominus$.
- Uranium (U) is the heaviest naturally occurring element.
- Plutonium (Pu) is the most poisonous element.
- Caesium (Cs) has the lowest EN and lightest liquid metal.
- Tellurium (Te) is the most stable element.
- Boron (B) is the lightest solid non-metal with highest tensile strength.
- Among non-metals sulphur (S_8) is the most poorest conductor of current.
- Osmium (Os) is the heaviest solid metal with density (22.57 g mL^{-1}).

1.1 INTRODUCTION

'The periodic table of elements is one of the most powerful icons in science—a single document that consolidates much of our knowledge of chemistry.'

The elements are arranged in rows and columns. Knowing the position of an element in the periodic table, it is possible to predict its chemistry.

Thus, a periodic table is defined as the table which classifies all the elements in such a way that elements with similar properties are grouped together in the same vertical column and elements with dissimilar properties are separated from one another.

1.2 GENESIS OF PERIODIC CLASSIFICATION: FROM DÖBEREINER TO MENDELEEV

Several chemists tried to classify the elements and to find patterns in their properties. The German chemist, Johann Döbereiner, in 1817, suggested that there were sets of three elements (triads) which showed similar chemical properties. In each case, he observed that the atomic weight of the central element of the triads was approximately the mean of the atomic weights of other two elements (Table 1.1) and the properties of the middle elements were in between those of the other two members. This relationship referred to as the *law of triads*. However, it was dismissed later on since it worked only for a few elements.

Table 1.1 Döbereiner's triads

	Elements	At. wt.	Mean of Ist and 3rd	Elements	At. wt.	Mean of Ist and 3rd	Elements	At. wt.	Mean of Ist and 3rd
1.	Li	7	$\frac{7+39}{2} = 23$	Ca	40	$\frac{40+137}{2} = 88.5$	Cl	35.5	$\frac{35.5+127}{2} = 81.25$
2.	Na	23		Sr	88		Br	80	
3.	K	39		Ba	137		I	127	

In 1862, a French geologist, A.E.B. de Chancourtois, arranged the then known elements in order of *increasing atomic weights* and made a cylindrical table of elements to show the periodic recurrence of properties. This also was dismissed later on.

1.2.1 Newlands' Octaves Law (1865)

However in 1865, the English chemist, John Alexander Newlands developed the *law of octaves*. He arranged the elements in increasing order of their *atomic weights* and found that every eighth element had properties similar to that of the first element (Table 1.2).

Table 1.2 Newlands' octaves

Elements	Li	Be	B	C	N	O	F
Atomic weight	7	9	11	12	14	16	19
Elements	Na	Mg	Al	Si	P	S	Cl
Atomic weight	23	24	27	29	31	32	35.5
Elements	K	Ca					
Atomic weight	39	40					

The relationship was just like every eighth note resembles the first octaves of music (Table 1.3).

Table 1.3

Sa	re	ga	ma	pa	dha	ni	sa
Li	Be	B	C	N	O	F	Na
Na	Mg	Al	Si	P	S	Cl	K

Note:
i. Inert gases were not discovered till that time.
ii. All elements could not be classified on this basis.

Law of octaves was found to be true up to calcium but this law was not widely accepted. However, this law was recognised much later by the Royal Society, London, by awarding Newlands the Davy Medal in 1887.

A breakthrough in the development of the periodic table owes its development to the Russian chemist Dmitri Mendeleev (1834–1907) and the German chemist Lothar Meyer (1830–1895).

Working independently, both the scientists in 1869 proposed that on arranging elements in the increasing order of their atomic weights, similarities appear in physical and chemical properties at regular intervals.

1.2.2 Lothar Meyer's Atomic Volume Curve (1869)

- Lothar Meyer plotted the physical properties such as atomic volume (i.e. atomic weight in solid state/density), melting points and boiling points against atomic weights.
- He observed elements with similar properties occupied the similar positions on the graph, i.e. a periodically repeated pattern.
- Elements of the 1st group (strong electropositive elements) such as Li, Na, K, Rb, Cs etc., occupied the top position.
- Elements of the 2nd group such as Be, Mg, Ca, Sr, Ba etc., occupied the positions on the ascending part of the graph.
- Halogens occupied the positions on the descending part of the graph.
- Inert gases except helium (He) also occupied the positions on the descending part of the graph.

1.2.3 Mendeleev's Periodic Law

By 1868, Lothar Meyer had developed a table that closely resembles the modern periodic table. However, his work was not published until the work of Mendeleev.

Döbereiner initiated the study of periodic relationship but Mendeleev published the periodic law for the first time. It states as follows:

- The physical and chemical properties of elements are periodic functions of their atomic weights.

- If the elements are arranged in the order of their increasing atomic weights, after a regular interval similar properties of elements are repeated.

Mendeleev's system of classifying elements was more elaborate than that of Lothar Meyer's. Mendeleev relied on the similarities in the empirical formulas and properties of the compounds formed by the elements. He found that some of the elements did not fit in with his scheme of classification if the order of atomic weight was strictly followed. So, he ignored the order of atomic weights and placed the elements with similar properties together.

For example, iodine with lower atomic weight (126.90) than that of tellurium (127.60, group VI) was placed in group VII along with F, Cl, Br because of similarities in properties.

While arranging the elements of similar properties in the same group, Mendeleev noticed that some of the elements were still undiscovered and, therefore, left several gaps in the table.

For example, both gallium (Ga) and germanium (Ge) were unknown at that time. He left the gap under aluminium and a gap under silicon and called these element *Eka-aluminium* and *Eka-silicon*. Besides predicting the existence of these elements he also predicted some of their physical properties. These elements were discovered later on. Some of the properties predicted by Mendeleev for these elements and those found experimentally are given in Table 1.4. Mendeleev's periodic table was published in 1905.

Mendeleev's name has been immortalised by naming the element with atomic number 101, as Mendelevium (Md).

Table 1.4 Mendeleev's predictions for the elements Eka-aluminium (Gallium) and Eka-silicon (Germanium)

Property	Eka-aluminium (predicted)	Gallium (found)	Eka-silicon (predicted)	Germanium (found)
Atomic weight	68	70	72	72.6
Density (g cm^{-3})	5.9	5.94	5.5	5.36
Melting point/K	Low	29.78	High	1231
Formula of oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
Formula of chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$

1.2.4 Mendeleev's Periodic Table

Mendeleev arranged the 63 discovered elements in the periodic table into 7 horizontal rows known as periods and 8 vertical columns known as groups numbered 1 to 8.

1.2.4.1 Uses of Mendeleev's Periodic Table

1. Atomic weights of elements were determined with the help of periodic table. Atomic weight = valency × equivalent weight.
2. Atomic weights of elements were corrected. Atomic weight of Be was calculated to be 3 × 4.5 = 13.5 by considering valency 3, but Mendeleev calculated it to be 2 × 4.5 = 9.
3. Discovery of new elements: In Mendeleev's periodic table two consecutive members differ by two or three units in the atomic weight. Where this gap was more, the gaps were left in the periodic table.
4. The discovery of the first two noble gases helium (He) and argon (Ar) in 1890 suggested the possibilities that there must be other similar elements to fill an entire family. This idea led Ramsay to his successful search for krypton (Kr) and xenon (Xe).
5. Work on the radioactive decay series for uranium (U) and thorium (Th) was also guided by the periodic table.

1.2.4.2 Defects of Mendeleev's Periodic Table

The following is a list of defects:

1. Position of hydrogen is uncertain. It has been placed in IA and VIIA groups because of its resemblance with both the groups.
2. No separate positions given for isotopes.
3. No separate group for lanthanides and actinides.
4. Although there is no resemblance expect valency of subgroups A and B, they have been put in the same group.
5. The order of increasing atomic weights is not strictly followed in the arrangement of elements in the periodic table. For example, Co (At.wt. 58.9) is placed before iodine (At.wt. 127) and Ar (At.wt. 39.9) before K (At.wt. 39).

1.3 MODERN PERIODIC LAW AND THE PRESENT LONG FORM OF THE PERIODIC TABLE OR MOSELEY'S PERIODIC TABLE

In 1913, the English physicist, Henry Moseley observed regularities in the characteristics X-ray spectra of the elements. Moseley studied the frequency (ν) of X-rays produced by the bombardment of a strong beam of electrons on a metal target. He found that a plot of $\sqrt{\nu}$ (where ν is the frequency of X-rays emitted) against the atomic number or nuclear charge (Z) gave a straight line and not the plot of $\sqrt{\nu}$ versus atomic mass, and gave the following relation:

$$\sqrt{\nu} = a(Z - b)$$

where a and b are constants. So, Moseley related the properties of elements with their atomic numbers and gave the new periodic law, known as the *Modern Periodic Law*, and is defined as:

The physical and chemical properties of elements are periodic functions of their atomic numbers.

If the elements are arranged in order of their increasing atomic numbers, after a regular interval, elements with similar properties are repeated.

The periodic law has stimulated renewed interest in inorganic chemistry and has carried till date with the creation of artificially produced short half-life elements.

The periodic law has also revealed important similarities among the 94 naturally occurring elements. For example, neptunium (Np) and plutonium (Pu) like actinium (Ac) and protoactinium (Pa) are also found in pitch blende—an ore of uranium (U).

It is now recognised that the periodic law is the consequence of the periodic variation in electronic configurations which determine the physical and chemical properties of elements and their compounds.

Although numerous forms of periodic table have been made. Out of which some forms emphasise chemical reactions and valence, whereas others emphasise the electronic configurations of elements. But the '*long form*' of the *periodic table* of the elements (Fig. 1.1) (or modern periodic table) is the most easy and widely used.

The horizontal rows (which Mendeleev called **series)** are called **periods** and the vertical columns, **groups**. Elements having similar outer electronic configurations in their atoms are arranged in vertical columns, referred to as **groups or families**. According to the recommendation of International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18 replacing the older notation of groups IA... VIIA, VIII, IB ... VIIB and O.

There are altogether seven periods. The period number corresponds to the highest principal quantum number (n) of the elements in the period. The first period contains 2 elements. The subsequent periods consist of 8, 8, 18, 18 and 32 elements, respectively. The seventh period is incomplete and like the sixth period would have a theoretical maximum (on the basis of quantum numbers) of 32 elements. In this form of the periodic table, 14 elements of both the sixth and seventh periods (lanthanoids and actinoids, respectively) are placed in separate panels at the bottom.

1.3.1 Magic Numbers

The examination of the properties of elements shows that the atomic number intervals at which the elements with similar properties reappear are 2, 8, 8, 18, 32 and 32, i.e. we have to pass 2, 8, 8, 18, 18 and 32 elements before we come across an element,with similar properties. The repetition of the elements with similar properties in the order of increasing atomic number as in the periodic table is called periodicity of properties and the numbers 2, 8,18 and 32 are called magic numbers.

Note: Glenn T. Seaborg's work starting with the discovery of plutonium in 1940 followed by those of all the transuranium elements from 94 to 102 led to reconfiguration of the periodic table placing the actinoids below the lanthanoids. In 1951, Seaborg was awarded the Nobel Prize in Chemistry for his work. Element 106 has been named Seaborgium (Sg) in his honour.

1.3.2 Electronic Configuration in Periodic Table

The following is a list of electronic configuration:

1. Each period starts with an alkali metal whose outermost electronic configuration is ns^1.
2. Each period ends with a noble gas of outermost electronic configuration ns^2np^6 except He. The electronic configuration of He is $1s^2$.
3. The number of elements in a period is equal to the number of necessary electrons to acquire ns^2np^6 configuration in the outermost shell of the first element (alkali metal) of the period. First period contains two elements.
4. The number of elements in each period may be determined by the number of electrons in a stable configuration.

1.4 NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBER > 100

The naming of the new elements was given traditionally on the name of its discoverer (or discoverers) and the suggested name was ratified by the IUPAC. In recent years this has led to some controversies. For example, both the American and Soviet scientists claimed credit for discovering element 104. The Americans named it *Rutherfordium* whereas the Soviets named it *Kurchatovium*.

To avoid such controversies, the IUPAC has made recommendation that until a new element's discovery is proved, and its name is officially recognised, a systematic nomenclature be derived directly from the atomic number using the numerical roots for O and numbers 1–9. These are shown in Table 1.5.

The roots are strung together in the order of digits which makes up the atomic numbers and 'ium' is added at the end. The IUPAC names for elements with Z above 103 are shown in Tables 1.5 and 1.6. As of now, elements with atomic numbers up to 112,114 and 116 have been discovered. Elements with Z = 113, 115 117 and 118 and beyond are not yet known.

Table 1.5 Notation for IUPAC nomenclature of elements

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

Represent-ative elements Group number

d-Transition elements

Representative elements

Noble gases

Period number	1 IA	2 IIA	3 III A	4 IV A	5 V A	6 VI A	7 VII A	8	9 VIII	10	11 IB	12 IIB	13 III B	14 IV B	15 VB	16 VI B	17 VII B	18 0
1	1 H $1s^1$																	2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$	27 Co $3d^74s^2$	28 Ni $3d^84s^2$	29 Cu $3d^{10}4s^1$	30 Zn $3d^{10}4s^2$	31 Ga $4s^24p^1$	32 Ge $4s^24p^2$	33 As $4s^24p^3$	34 Se $4s^24p^4$	35 Br $4s^24p^5$	36 Kr $4s^24p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$	45 Rh $4d^85s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10}5s^1$	48 Cd $4d^{10}5s^2$	49 In $5s^25p^1$	50 Sn $5s^25p^2$	51 Sn $5s^25p^3$	52 Te $5s^25p^4$	53 I $5s^25p^5$	54 Xe $5s^25p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $5d^16s^2$	72 Hf $4f^{14}5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$	77 Ir $5d^76s^2$	78 Pt $5d^96s^1$	79 Au $5d^{10}6s^1$	80 Hg $5d^{10}6s^2$	81 Tl $6s^26p^1$	82 Pb $6s^26p^2$	83 Bi $6s^26p^3$	84 Po $6s^26p^4$	85 At $6s^26p^5$	86 Rn $6s^26p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $6d^17s^2$	104 Rf $5f^{14}6d^27s^2$	105 Db $6d^37s^2$	106 Sg $6d^47s^2$	107 Bh $6d^57s^2$	108 Hs $6d^66s^2$	109 Mt $6d^77s^2$	110 Ds $6d^87s^2$	111 Rg $6d^{10}7s^2$	112 Cn $6d^{10}7s^2$	113 Nh $7s^27p^1$	114 Fl $7s^27p^2$	115 Mc $7s^27p^3$	116 Lv $7s^27p^4$	117 Ts $7s^27p^5$	118 Og $7s^27p^6$

f-inner transition elements

*Lanthanoids $4f^n5d^{0-1}6s^2$	58 Ce $4f^25d^0$ $6s^2$	59 Pr $4f^35d^0$ $6s^2$	60 Nd $4f^45d^0$ $6s^2$	61 Pm $4f^55d^0$ $6s^2$	62 Sm $4f^65d^0$ $6s^2$	63 Eu $4f^75d^0$ $6s^2$	64 Gd $4f^75d^1$ $6s^2$	65 Tb $4f^95d^0$ $6s^2$	66 Dy $4f^{10}5d^1$ $6s^2$	67 Ho $4f^{11}5d^0$ $6s^2$	68 Er $4f^{12}5d^0$ $6s^2$	69 Tm $4f^{13}5d^0$ $6s^2$	70 Yb $4f^{14}5d^0$ $6s^2$	71 Lu $4f^{14}5d^1$ $6s^2$
**Actinoids $5f^n6d^{0-2}7s^2$	90 Th $5f^06d^2$ $7s^2$	91 Pa $5f^26d^1$ $7s^2$	92 U $5f^36d^1$ $7s^2$	93 Np $5f^46d^1$ $7s^2$	94 Pu $5f^66d^1$ $7s^2$	95 Am $5f^76d^0$ $7s^2$	96 Cm $5f^76d^0$ $7s^2$	97 Bk $5f^96d^0$ $7s^2$	98 Cf $5f^{10}6d^0$ $7s^2$	99 Es $5f^{11}6d^0$ $7s^2$	100 Fm $5f^{12}6d^0$ $7s^2$	101 Md $5f^{13}6d^0$ $7s^2$	102 No $5f^{14}6d^0$ $7s^2$	103 Lr $5f^{14}6d^1$ $7s^2$

Fig. 1.1 Long form of the periodic table of the elements with their atomic numbers and ground state outer electronic configurations. The groups are numbered 1–18 in accordance with the 1984 IUPAC recommendations. This notation replaces the old numbering scheme of IA–VII A, VIII, IB–VIIB and 0 for the elements.

*** A more detailed periodic table is given at the book end.**

Table 1.6 Nomenclature of elements with atomic number above 100

At. no.	Name	Symbol	IUPAC official name	IUPAC symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassnium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnilium	Uun	Darmstadium	Ds
111	Unununium	Uuu	Rontgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	Nihonium	Nh
114	Ununquadium	Uuq	Flerovium	Fl
115	Ununpentium	Uup	Moscovium	Mc
116	Ununhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	Tennessine	Ts
118	Ununoctium	Uuo	Oganesson	Og

Thus, the new element first gets a temporary name, with symbol consisting of three letters. Later on a permanent name and a symbol are given by a process of voting of the IUPAC representatives from each country. The permanent name might reflect the country (or the state of the country) in which the element was discovered, or pay tribute to a notable scientist.

ILLUSTRATION 1.1

What would be the IUPAC name and symbol for the element with atomic number 120?

Sol. From Table 1.5, the roots for 1, 2 and 0 are Un, bi and nil, respectively. Hence, the symbol and the name respectively are Ubn and unbinilium.

ILLUSTRATION 1.2

There are 2, 8 and 8 elements in the first, second and third periods of periodic table respectively. Explain.

Sol. The first period ($1s$) is completed with two electrons. The second period ($2s$, $2p$) is completed with 2 and 6 electrons respectively in $2s$ and $2p$.

Likewise the third period ($3s$, $3p$) is completed with 2 and 6 electrons. Thus, 2, 8 and 8 elements are present in the first, second and third periods respectively.

ILLUSTRATION 1.3

Which of the following is correct:

a. The element Mendelevium (Md) has been named in the honour of Mendeleev. What is the atomic number of that element?

i. 100 ii. 101 iii. 102 iv. 103

b. The element Seaborgium (Sg) has been named in the honour of Glenn T. Seaborg. What is the atomic number of that elements?

i. 104 ii. 105 iii. 106 iv. 107

c. Glenn T. Seaborg was awarded Nobel Prize in 1951 for the discovery of which element/elements?

i. Uranium (U)
ii. Elements from 90 to 93
iii. Elements from 94 to 102
iv. Elements from 103 to 106

Sol. **a.** ii **b.** iii **c.** iii

ILLUSTRATION 1.4

a. What is the atomic numbers and the IUPAC name and symbol for the elements Mendelevium (Md) and Seaborgium (Sg)?

b. What is the atomic number of the element for which both the American and Soviet scientists claimed credit for the discovery?

c. Refer to the problem (b) above, what name is given to the above element by the American and Soviet scientists?

d. Which other elements are found in pitch blende–an ore of uranium?

e. Which other elements are found in the naturally occurring element with atomic number 94?

Sol.

a. i. Atomic number for Mendelevium is 101. Its IUPAC name and symbol is Unnilunium (Unu).

ii. Atomic number for Seaborgium is 106. Its IUPAC name and symbol is Unnilhexium (Unh).

b. Atomic number of that element is 104.

c. The American scientist called it Rutherfordium (Rf) and the Soviet scientist called it Kurchatovium.

d. Actinium (Ac) and Protoactinium (Pa).

e. Neptunium (atomic number 93) and plutonium (atomic number 94).

1.5 ELECTRONIC CONFIGURATIONS OF ELEMENTS AND THE PERIODIC TABLE

An electron in an atom is characterised by a set of four quantum numbers, and the principal quantum number (n) defines the main energy level known as shell. The filling of electrons into different subshells, also referred to as orbitals (s, p, d, f) in an atom, is called its electronic configuration.

1.5.1 Electronic Configurations Across Periods

The period indicates the value of n for the outermost or valence shell. In other words, successive period in the periodic table is associated with the filling of the next higher principal energy level ($n = 1$, $n = 2$ etc.). We know that the number of elements in each period is twice the number of atomic *orbitals* available in the energy level that is being filled.

The first period ($n = 1$) starts with the filling of the lowest level ($1s$) and therefore has two elements—hydrogen ($1s^1$) and helium ($1s^2$) when the first shell (K) is completed.

The second period ($n = 2$) starts with lithium and the third electron enters the $2s$ orbital.

The next element, beryllium, has four electrons and has the electronic configuration $1s^22s^2$.

In the next element, boron, the $2p$ orbitals are filled with electrons when the L shell is completed at neon ($2s^2p^6$). Thus, there are 8 elements in the second period.

The third period ($n = 3$) begins at sodium, and the added electron enters a $3s$ orbital. Successive filling of $3s$ and $3p$ orbitals gives rise to the third period of 8 elements from sodium to argon.

The fourth period ($n = 4$) starts at potassium, and the added electrons fill up the $4s$ orbital. Now before the $4p$ orbital is filled, filling up of $3d$ orbitals becomes energetically favourable and *3d transition series* of elements begins. This starts from scandium ($Z = 21$) which has the electronic configuration $3d^1\,4s^2$. The $3d$ orbitals are filled at zinc ($Z = 30$) with electronic configuration $3d^{10}4s^2$.

The fourth period ends at krypton with the filling up of the $4p$ orbitals. Altogether there are 18 elements in this fourth period.

The fifth period ($n = 5$) begins with rubidium is similar to the fourth period and contains the *4d transition series* starting at yttrium ($Z = 39$). This period ends at xenon with the filling up of the $5p$ orbitals.

The sixth period ($n = 6$) contains 32 elements and successive electrons enter $6s$, $4f$, $5d$ and $6p$ orbitals, in the order of filling up of the $4f$ orbitals begins with cerium ($Z = 58$) and ends at lutetium ($Z = 71$) to give the **4*f* inner transition series** which is called the **lanthanoid series**.

The seventh period ($n = 7$) is similar to the sixth period with the successive filling up of the $7s$, $5f$, $6d$ and $7p$ orbitals and includes most of the man-made radioactive elements. This period will end at the element with atomic number 118 which would belong to the noble gas family.

Filing up of the $5f$ orbitals after actinium ($Z = 89$) gives the **5*f* inner transition** series known as the **actinoid series**. The $4f$ and **5*f* inner transition** *series* of elements are placed separately in the periodic table to maintain its structure and to preserve the principle of classification by keeping elements with similar properties in a single column.

The number of elements in a period and the type of orbitals being filled up is given in Table 1.7.

Table 1.7 Number of elements in different periods

Period	Number of energy level being filled	Orbitals being filled	Number of orbitals	Number of electrons or elements in the period
1	$n = 1$	$1s$	one s	2
2	$n = 2$	$2s$, $2p$	one s + three $p = 4$	$2 + 6 = 8$
3	$n = 3$	$3s$, $3p$	one s + three $p = 4$	$2 + 6 = 8$
4	$n = 4$	$4s$, $3d$, $4p$	one s + five d + three $p = 9$	$2 + 10 + 6 = 18$
5	$n = 5$	$5s$, $4d$, $5p$	one s + five d + three $p = 9$	$2 + 10 + 6 = 18$
6	$n = 6$	$6s$, $4f$, $5d$, $6p$	one s + seven f + five d + three $p = 16$	$2 + 14 + 10 + 6 = 32$
7	$n = 7$	$7s$, $5f$, $6d$, $7p$	one s + seven f + five d + three $p = 16$	$2 + 14 + 10 + 6 = 32$. In this period only 29 elements are known so far.

The first three periods (1st, 2nd and 3rd) containing 2, 8 and elements, respectively, are known as **short periods** while the ne three periods (4th, 5th and 6th) containing 18, 18 and 32 element respectively, are called **long periods.**

ILLUSTRATION 1.5

How would you justify the presence of 18 elements in the 5th period of the periodic table?

Sol. When $n = 5$, $l = 0, 1, 2, 3$ and 4. The order in whic the energy of the available orbitals $4d$, $5s$ and $5p$ increases $5s < 4d < 5p$. The total number of orbitals available is 9. Th maximum number of electrons that can be accommodated is 18 and therefore 18 elements are there in the 5th period.

1.5.2 Groupwise Electronic Configurations

Elements in the same vertical column or group have similar valenc shell electronic configurations, the same number of electrons i the outer orbitals, and similar properties. For example, the Grou 1 elements (alkali metals) have ns^1 valence shell electroni configuration.

Thus, it can be seen that the properties of an element hav periodic dependence upon its atomic number and not on relativ atomic mass.

1.6 ELECTRONIC CONFIGURATIONS AND TYPE OF ELEMENTS: s-, p-, d-, and f-BLOCKS

The Aufbau (build up) principle and the electronic configuratio of atoms provide a theoretical foundation for the periodi classification. The elements in a vertical column of the periodi table constitute a group or family and exhibit similar chemica

behaviour. This similarity arises because these elements have the same number and same distribution of electrons in their outermost orbitals. The elements are classified into four blocks *viz.* **s-block, p-block, d-block** and **f-block** depending on the type of atomic orbitals that are being filled with electrons (Fig. 1.2).

There are two exceptions to this categorisation. Helium belongs to the *s*-block but its positioning in the *p*-block along with other group 18 elements is justified because it has a completely filled valence shell ($1s^2$) and as a result, exhibits properties characteristic of other noble gases.

The other exception is hydrogen. It has a lone *s*-electron and hence can be placed in group 1 (alkali metals). It can also gain an electron to achieve a noble gas arrangement and hence it can behave similar to a group 17 (halogen family) elements. But Mendeleev placed it at the top of the periodic table as shown in Fig. 1.1 and hydrogen separately.

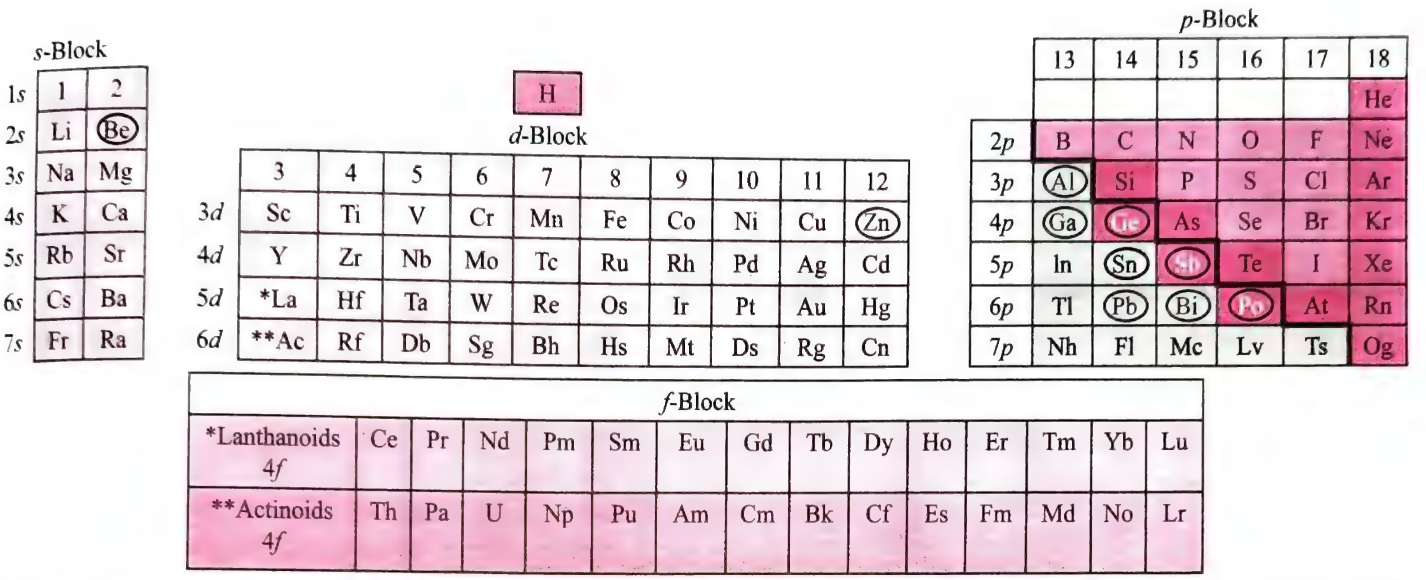


Fig. 1.2 The types of elements in the periodic table based on the orbitals that are being filled. Also shown is the broad division of elements into metals ( ), non-metals ( ) and metalloids ( ). Elements in circle shown their compounds are amphoteric in nature.

1.6.1 Merits of Long Form of Periodic Table over Mendeleev's Periodic Table

The merits of the long form of periodic table are as follows:

1. The classification of the elements is based on more fundamental property i.e. atomic number.
2. It relates the position of an element to its electronic configuration. Thus, each group contains elements with similar electronic configuration and hence similar properties. For example, all the alkali metals have similar valence shell electronic configuration i.e. ns^1 configuration and hence have similar properties.
3. The inert gases having completely filled electron shells have been placed at the end of each period, which represents a logical completion of each period.
4. The elements of the two subgroups have been placed separately and thus dissimilar elements do not fall together.
5. It provides a clear demarcation of different types of the elements such as active metals, transition elements, non-metals, metalloids, inert gases, lanthanides and actinides.
   a. Active metals (groups 1 and 2) are located at the extreme left of the periodic table.
   b. Transition metals are placed in the middle of the table.
   c. The elements lying to the right of the dark line, shown in Fig 1.2. in the form of a ladder (i.e. steps) are noble gases and non-metals while those lying to the left of the dark line are metals (active metals and transition metals).

   The elements shown in the circle are metalloids and their oxides are amphoteric, in the decreasing order as shown.

   Be > B > Al > Ge > Ga > Zn > Sb > Sn > Bi > Pb

   Pb is the least amphoteric and its oxides are almost acidic.
6. It is easier to remember, understand and reproduce.

1.6.2 Defects of Long Form of Periodic Table

Although the long form of the periodic table is superior to Mendeleev's periodic table in many respects, yet it has some defects:

1. Like Mendeleev's table, it fails to accommodate the lanthanides and actinides in the main body of the table.
2. Position of hydrogen is not solved though it can be placed along with alkali metals in group 1 and halogens in group 17, since it shows many properties similar to both alkali metals and halogens.
3. The arrangement is unable to reflect the electronic configuration of many elements.

1.6.3 The *s*-Block Elements

The elements of group 1 (alkali metals) and group 2 (alkaline earth metals) which have ns^1 and ns^2 outermost electronic configuration belong to the *s-block elements*. They are all reactive metals with low ionisation enthalpies. They lose the outermost electon(s) readily to form +1 (in the case of alkali metals) or +2 ions (in

the case of alkaline earth metals). The metallic character and the reactivity increase as we go down the group. The compounds of the *s*-block elements, with the exception of those of beryllium are predominantly ionic.

1.6.3.1 Characteristics of *s*-Block Elements

1. They have the common group valency of +1 and +2 for group 1 and 2 respectively.
2. They are malleable and ductile.
3. They are good conductors of heat and electricity.
4. They are prepared by the electrolysis of their fused compounds.
5. Chemically they are very reactive as their last shell contains only 1 or 2 electrons which can be given out easily.
6. They have low ionisation potential.
7. They form ionic compounds (except lithium and beryllium).
8. They are diamagnetic and form colourless compounds except chromates, permanganates and dichromates.
9. They are good reducing agents.

Note: The above properties are not applicable to hydrogen.

1.6.4 The *p*-Block Elements

The *p-block elements* comprise those belonging to groups 13 to 18 and together with the *s*-block elements are called the representative elements or normal or main group elements. The outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period. Each period ends in a noble gas with a closed shell ns^2np^6 configuration. All the orbitals in the valence shell of the *noble gases* are completely filled by electrons and it is very 'difficult to alter this stable arrangement by the addition or removal of electrons. The noble gases thus exhibit very low chemical reactivity. Preceeding the noble gas family are two chemically important groups of non-metals. They are the *halogens* (group 17) and the *chalcogens* (group 16). These two groups of elements have high negative electron gain enthalpies and readily add one or two electrons, respectively, to attain the stable noble gas configuration. The non-metallic character increases as we move from left to right across a period (→) and metallic character increases as .we go down the group (↓).

1.6.4.1 Characteristics of *p*-Block Elements

1. They have variable valencies and oxidation states, e.g. +3 and +5.
2. Most of them are electronegative.
3. Most of them are non-metals.
4. They are bad conductors of heat and electricity (except metals).
5. They form both covalent and ionic bonds.
6. The non-metallic oxides are acidic in character, e.g. NO_2, P_2O_5, SO_3 etc.
7. They form both coloured and colourless compounds.
8. Most of the non-metals have polyatomic molecules.

1.6.5 The *d*-Block Elements (Transition Elements)

These are the elements of group 3 to 12 in the centre of the periodic table. These elements are characterised by the filling of the inner *d* orbitals by electrons and are therefore referred to as *d*-block elements. These elements have the outer electronic configuration $(n-1)\,d^{1-10}\,ns^{1-2}$. They are all metals and mostly form coloured ions. But Hg which has the $(n-1)d^{10}\,ns^2$ electronic configuration does not show most of the properties of transition elements. In a way, transition metals form a bridge between the chemically active metals of *s*-block elements and the less active metals of groups 13 and 14 and thus take their familiar name 'transition elements'.

1.6.5.1 Characteristics of *d*-Block Elements

1. They have variable valencies and oxidation states, e.g. Fe(II), Fe(III), Cu(I), Cu(II), Mn(II), Mn(IV), Mn(VI) and Mn(VII).
2. They are malleable and ductile.
3. They are hard and have high density and melting point.
4. They are good conductors of heat and electricity.
5. They form ionic compounds as well as giant molecules and complexes in which they are covalent.
6. They are paramagnetic since they contain unpaired electrons (each electron acts as a small magnet).
7. They form coloured compounds and coloured complexes. They have vacant orbitals. Electrons take up energy and move to higher energy levels and thus appear coloured.
8. They have higher ionisation potential than *s*-block elements.

   Note: Those d-block elements which have partially filled d-orbitals or form ions in which the d-orbitals are only partially filled, have some special characteristics and are defined as transition elements or metals. Exceptions are Zn, Cd and Hg. Zn has all the d-orbitals completed both in the metal atoms and in Zn^{2+} ions.

$$_{30}Zn = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2$$
$$_{48}Cd = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,5s^2$$
$$_{80}Hg = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,4f^{14}\,5s^2\,5p^6\,5d^{10}\,6s^2$$

II B group metals cannot be included in transition metals. Other exceptions are Sc and Cu, where Cu shows intermediate behaviour since it forms compounds in two oxidation states $Cu^{\oplus}$ and Cu^{2+}. The latter ion is transition metal ion.

1.6.6 The *f*-Block Elements (Inner-Transition Elements)

The two rows of elements at the bottom of the periodic table, called the *lanthanoids* $_{58}Ce$–$_{71}Lu$ and *actinoids* $_{90}Th$–$_{103}Lr$ are characterised by the outer electronic configuration $(n-2)f^{1-14}\,(n-1)d^{0-1}\,ns^2$. The last electron added to each elements is an *f*-electron. These two series of elements are hence called the inner transition elements (*f-block elements*). They are all metals. Within each series, the properties of the elements are quite similar. The chemistry of the early actinoids is more complicated than the

corresponding lanthanoids, due to the large number of oxidation states possible for these actinoid elements.

1.6.6.1 Characteristics of f-Block Elements

1. All are metals.
2. They show variable valency. The +3 is the most important oxidation state. Few elements show +2 and +4 oxidation states.
3. They are paramagnetic in nature.
4. They form coloured compounds.
5. They have tendency to form complexes.
6. Chemically, lanthanides are very similar. It is difficult to separate them from a mixture by application of a chemical property. Similary, actinides have similar chemical properties. The members of actinides show the phenomenon of radioactivity. Elements above atomic number 92 are called transuranium elements (Z = 94 to 102) and are not found in nature. These are man-made.
   They are obtained in nanogram or even less by nuclear reactions.

For names and shapes of *f*-orbitals, refer to the table and figure given in Example 1.35.

1.6.7 Inert Gases

The elements which belong to the 0 (zero) group of the periodic table are known as inert gases. They have 8 electrons (except helium) in their outermost shell. Therefore, their combining capacity (valency) is zero. Hence, they are inert in nature. However, it was discovered recently that they form a number of compounds with the most electronegative element, fluorine. In inert gases, atomic radii are very large. Interatomic forces are weak since electrons are paired. They exist in monoatomic state.

Elements in the long form of the periodic table have been divided into four blocks i.e. *s*, *p*, *d* and *f*, based upon the name of orbitals in which the last electron enters. These are shown in Table 1.8.

Table 1.8 Division of periodic table into *s*, *p*, *d* and *f*-blocks

s-Block elements		*p*-Block elements
ns^{1-2} (two groups)	Transition elements (*d*-Block elements) $(n-1)d^{1-10}ns^{0-2}$ (ten groups)	$ns^2\,np^{1-6}$ (six groups)
Transition and inner transition elements. lanthanides and actinides. *f*-Block elements: $(n-2)f^{0-14}\,(n-1)d^{0-1}\,ns^2$.		

1.7 METALS, NON-METALS AND METALLOIDS

The elements can be further divided into metals, non-metals and metalloids (see Fig. 1.2).

1.7.1 Metals

1. The constituent particles of metals are atoms held together by the bonds called metallic bonds.
2. They comprise more than 78% of all known elements.
3. They appear on the left side of the *periodic table*.
4. They usually have high melting and boiling points.
5. They as usually solids at room temperature (except mercury (Hg)). Gallium (Ga) and cesium (Cs) have low melting points (303 K and 302 K).

   Note: Due to low melting point and high boiling point of Ga, it is used in making high temperature thermometer.
6. They are good conductors of heat and electricity.
7. They are malleable (can be flattened into thin sheet by hammering) and ductile (can be drawn into wires).

1.7.2 Non-Metals

1. They are located at the right side of the *periodic table*.
2. In a horizontal row, the property of elements changes from metallic on the left to non-metallic on the right.
3. They are poor conductors of heat and electricity.
4. Mostly they are brittle and are neither malleable nor ductile.
5. Down the group, the metallic character increases and non-metallic character increases along the period (i.e., as one goes from the left to the right).
6. They are usually solids or gases at room temperature with low melting and boiling points [except boron (B) and carbon (C)].

Note: Boron has the highest melting point in its group because boron exist as B_{12} (icosahedron structure).

1.7.3 Metalloids or Semi-Metals

They show properties that are characteristics of both metals and non-metals. The change from metallic to non-metallic character is not abrupt as shown by the thick zig-zag line in Fig. 1.2.

For example, the elements, i.e. silicon (Si), germanium (Ge), arsenic (As), antimony (Sb) and tellurium (Te) bordering this line and running diagonally across the periodic table are metalloids.

Note: Ge is transparent in the infrared region and therefore is used in the making of infrared windows, prisms and lenses. Si is a very important component of ceramics, glass and cement. Si and Ge (though to lesser extent) are used in the production of semiconductors and integrated circuit.

1.7.4 Nature of Bonding in Metals

The bonding among metal atoms cannot be ionic, covalent or van der Waals types as explained below:

1. Taking the example of lithium, it is known that each lithium atom has eight nearest neighbours. Electronic configuration of Li is $1s^2 2s^1$ i.e. it has only one valence electron. Hence, the possibility of its forming electron pair covalent bonds with eight other atoms is ruled out.
2. Presence of only one kind of atoms in a metal without any electronegativity difference rules out the possibility of ionic bonding.
3. The fact that the metals are quite strong rules out the possibility of their being held together by the weak van der Waals forces.

1.7.5 ELECTRON SEA MODEL OR ELECTRON GAS MODEL

To explain the various characteristics of metals such as conductivity, lustre, melleability, ductility etc., a model called electron sea model or electron gas model has been put forward. According to this model, as metals have low ionisation energy, their valence electrons are held very loosely, i.e. they are almost like free electrons (Fig. 1.3).

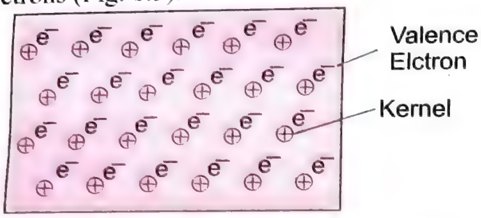


Fig. 1.3 Structure of metals (electron sea model)

All atoms contribute to form a pool of electrons which is mobile. Leaving the valence electrons, the remainder portion of the metal atom is a positive ion called 'kernel'. For example, in lithium, each atom contributes one valence electron to the pool leaving behind $Li^{\oplus}$ ions; in case of Mg, each atom contributes two valence electrons to the pool leaving behind Mg^{2+} ion. These positive ions or kernels are held in the three-dimensional space in a definite pattern in the sea of mobile electrons. This model is called electron gas model because the electrons are free to move in all directions like the molecules of a gas.

The simultaneous attraction between the kernels and the mobile electrons which holds the kernels together is called the metallic bond.

1.7.6 COMPARISON OF COVALENT BOND AND METALLIC BOND

A few important points of differences are as follows.

Covalent bond:

1. In a covalent bond, the valence electrons are localised between the atoms and hence it has a directional character.
2. Covalent bonds are quite stronger as the valence electrons in them are strongly attracted by the nuclei of the atoms.

Metallic bond:

1. In the metallic bond, the valence electrons are spread all over the crystal more or less uniformly. Hence, it is *non-directional in character.*
2. In this case, the valence electrons are mobile and are weakly attracted by the nuclei (kernels) and hence it is weaker.

1.7.7 CHARACTERISTICS OF METALS AND THEIR EXPLANATION BY ELECTRON SEA MODEL

The characteristic properties of metals and their explanation on the basis of electron gas model of the metallic bond are given below:

1. **Electrical conductivity**: Electrical conductivity of the metals is due to mobile electrons. In a metal crystal, the electrons are flowing equally in all directions. But when a potential difference is applied across a metal, there will be a directed flow of electrons towards the positive electrode. The directed flow of electrons carries the electric current from one point to another and, therefore, the metals are known to be good conductors.
2. **Effect of temperature on conductivity:** The conductivity of the metal decreases with the rise in temperature. This is because with the rise in temperature the positively charged kernels also start vibrating which interfere with the movement of electrons. As a result conductivity decreases.

   In metals, the electrons are the charge carriers while in ionic liquids the charge is carried by the ions. Further, the electrons are lighter than ions and hence are more mobile. It is because of this reason that the electrical conductivity of metals is much higher than the electrical conductivity of ions in liquids.
3. **Thermal conductivity:** Thermal conductivity of the metal is also due to mobile electrons. On heating a part of the metal, the kinetic energy of the electrons in that region increases. The energised electrons move rapidly to the cooler parts and give their excess kinetic energy to other electrons in the cooler part of the metal. Thus, the heat is conducted throughout the metal.
4. **Metallic lustre:** The bright metallic lustre is due to the delocalised mobile electrons. When light falls on the surface of a metal, the most loosely bound electrons absorb photons of a radiant energy of visible light. Consequently, the electrons start vibrating at a frequency equal to that of the incident light. The vibrating electrons emit electromagnetic radiations in the form of light. As such it appears as if light is being reflected from metal surface and the surface gains a shining appearance which is known as metallic lustre.
5. **Malleability and ductility:** Since the metallic bond is non-directional; metals can be twisted, drawn into wires or beaten into sheets. This is because the kernels can slip over each other when a deforming force is applied.

1.7.8 ELECTROPOSITIVE OR METALLIC CHARACTER

The alkaline earth metals are highly electropositive and hence metallic and their electropositive or metallic character increases down the group. However, they are less electropositive or metallic than the alkali metals.

Explanation: On account of their relatively low ionisation energies, the alkaline earth metals have a strong tendency to lose both the valency electrons to form dipositive cations. Thus, these elements show strong electropositive or metallic character.

Down the group (↓), the atomic radii increase and ionisation energies decrease. Consequently, the electropositive or metallic character increases.

Further, since the atoms of the alkaline earth metals have smaller size and higher ionisation energies as compared to the corresponding alkali metals, their tendency to lose valence electrons is lesser than those of alkali metals. Consequently alkaline earth metals have less electropositive or metallic character as compared to alkali metals.

Due to the smaller size of the kernel and greater number of valence electrons, the metallic bonding in alkaline earth metals is stronger as compared to alkali metals. Because of this reason, these metals are less soft (harder) than alkali metals.

1.7.9 Metallic Character of Transition Elements

All the transition elements are metals having *hcp*, *ccp* or *bcc* lattices. They exhibit all the characteristic of metals, e.g. they are hard, lustrous, malleable and ductile, have high melting and boiling points, high thermal and electrical conductivity and high tensile strength.

Explanation: Transition elements have relatively low ionisation energies and have one or two electrons in their outermost energy level (ns^1 or ns^2). As a result, metallic bonds are formed. Hence they behave as metals. The unpaired *d*-electrons also result in the formation of metallic bonds. Greater the number of unpaired *d*-electrons, stronger is the bonding due to the overlapping of unpaired electrons between different metal atoms. Cr, Mo and W have maximum number of unpaired *d*-electrons and are therefore hard metals whereas Zn, Cd and Hg are not very hard metals due to the absence of unpaired electrons.

1.7.10 Melting and Boiling Points

Transition metals have very high melting and boiling points. The melting points of the transition elements rise to a maximum and then fall as the atomic number increases. Manganese and technetium have abnormally low melting points.

Explanation: Strong metallic bonds between the atoms of these elements are responsible for the high melting and boiling points. This is clear from their high enthalpies of atomisation (i.e. heat required to break the metal lattice to get free atoms).

The strength of the metallic bond depends upon the number of unpaired *d*-electrons (half-filled *d*-orbitals). Greater is the number of unpaired electrons (half-filled orbitals) stronger is the metallic bonding. Because of the stronger metallic bonding, these elements have high melting and boiling points.

In a particular series, the metallic strength increases up to the middle with the increasing number of unpaired electrons, i.e. up to d^5 configuration (e.g. Sc has 1, Ti has 2, V has 3 and Cr has 5 unpaired electrons). After Cr the number of unpaired electrons goes on decreasing (e.g. Fe has 4, Co has 3 unpaired electrons and so on). Accordingly the melting points decrease after the middle of the increasing pairing of electrons.

As there are no unpaired electrons in Zn, Cd and Hg, they are soft and have low melting points. Hg is liquid at ordinary temperature with melting point of 234 K.

Decreasing order of metallic character is given below:

K > Na > Ba > Ca > Mg > Al > Zn > Fe > Ni > Sn > Pb $\boxed{H}$ > Cu > Hg > Ag > Au > Pt

The useful mnemonic to remember the metallic series is:

PSBC	MAZINTL	H	CHAAP
P = Potassium (K)	M = Magnesium (Mg)		C = Copper (Cu)
S = Sodium (Na)	A = Aluminium (Al)		H = Mercury (Hg)
B = Barium (Ba)	Z = Zinc (Zn)		A = Silver (Ag)
C = Calcium (Ca)	I = Iron (Fe)		A = Gold (Au)
	N = Nickel (Ni)		P = Platinum (Pt)
	T = Tin (Sn)		
	L = Lead (Pb)	Non-metal	

Note: That hydrogen is not a metal and comes between MAZINTL and CHAAP

ILLUSTRATION 1.6

Considering the atomic number position in the periodic table, arrange the following elements in the increasing order of metallic character: Si, Be, Mg, Na, P.

Sol. Metallic character increases down a group and decreases along a period as we move form the left to the right. Hence, the order of increasing metallic character is P < Si < Be < Mg < Na.

1.8 PREDICTION OF GROUP, PERIOD AND BLOCK OF A GIVEN ELEMENT

The group, period and block of any element can be predicted from its electronic configuration by the following ways:

1. Principal quantum number of the valence shell corresponds to the period of an element.
2. The orbital containing the last electron indicates the block of an element.
3. The group of an element is predicted from the number of electrons in the valence shell or a penultimate shell (n–1) as follows.
   a. For *s*-block elements, the group number is equal to the number of valence electrons.
   b. For *p*-block elements, the group number is equal to 10 + number of electrons in the valence shell.
   c. For *d*-block elements, the group number is equal to the number of electrons in (n – 1) *d*-subshell + number of electrons in valence shell (*n*th shell) Alternately one can calculate group number = number of electrons in (penultimate shell + valence shell) – 8.
   d. For *f*-block elements, the group number is always 3 or III B.

Note: The element with atomic number 103 is present in the 3rd group (or III B) and 7th period. Similarly, the element with atomic number 104 is present in the 4th group (or IV B) and 7th period. Likewise elements with atomic numbers from 105 to 118 are present in the 5th, 6th, 7th, 8th, 9th, 10th, 11th, 12th, and so on up to 18th group and all of them are present in the 7th period. Element with atomic number 119 again is present in the 1st or IA group and in 8th period and so on.

ILLUSTRATION 1.7

Predict the period, group number and block of the following elements. A (at. no. = 8), B (at. no. = 11), C (at. no. = 28) and D (at. no. = 54).

Sol. Electronic configurations of different elements are

$A \rightarrow 1s^2\ 2s^2\ 2p^4$

$B \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^1$

$C \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$

$D \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$

Element A: *p*-block element

Group number = 10 + number of electron in the valence shell = 10 + 6 = 16

Period of the element = Principal quantum number of the valence shell = 2nd.

Elements B: *s*-block element

Group number = Number of electrons in valence shell = 1

Period number = 3rd

Element C: *d*-block element

Group number = Number of electrons in penultimate shell and valence shell = 8 + 2 = 10

Period of the = Principal quantum number of the valence shell = 4th

Element D: *p*-block element

Group number = 10 + number of electron in the valence shell = 10 + 8 = 18

Period number = 5

ILLUSTRATION 1.8

What is the atomic number of the element having maximum number of unpaired 2*p* electrons? To which group it belongs?

Sol. $_7N$. It belongs to 15 (or VA gp) group

ILLUSTRATION 1.9

The elements Z = 117 and 120 have not yet been discovered. In which family/group would you place these elements and also give the electronic configuration in each case.

Sol. The elements with $Z = 117$ belong to the halogen family (group 17) and the electronic configuration is $[Rn]5f^{14}6d^{10}7p^5$. The elements with $Z = 120$ will be placed in group 2 (alkaline earth metals) and will have the electronic configuration $[Uuo]8s^2$.

ILLUSTRATION 1.10

Write the electronic configuration of the elements given below and also predict the block, group number and period to which they belong. (Z = Atomic number)

I. A (Z = 5), B (Z = 11), C (Z = 28), D (Z = 54), E (Z = 59), F (Z = 90).

II. Classify them as representative elements, transition, inner transition elements and noble gases.

Sol.

I. **Element A** ($Z = 5$): Name of element = Boron, (*B*) Electronic conjuration of A = $1s^2\ 2s^2\ 2p^1$

The last electron enters in 2*p* orbital, therefore it belongs to *p-block elements*

Group number = 10 + Number of electrons in the valence shell

= 10 + 3 = 13

Period of the element = Number of the principal quantum number of the valence shell = 2nd.

Element B ($Z = 11$): Name of element = sodium (Na)

Electronic configuration of B = $1s^2\ 2s^2 2p^6\ 3s^1$

The last electron is present in 3 *s*-orbital, therefore it belongs to *s-block elements*.

Group number = Number of electrons in the valence shell = 1

Period of the element = Number of the principal quantum number of shell = 3rd

Element C ($Z = 28$): (Name of element = Nickel) (Ni)

Electronic configuration of C: $1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 3d^8\ 4s^2$.

The last electron enters into 3*d*-orbital, therefore it belongs to *d-block elements*.

Group Number = Number of electrons in the penultimate shell + number of electrons in the valence shell = 8 + 2 = 10.

Period of the element: Number of principal quantum number of the valence shell = 4th.

Element D ($Z = 54$): Name of element = Xenon (Xe)

Electronic configuration: $1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$

The last electron is present is 5*p*-orbital, therefore it belongs to the *p-block elements*.

Group number = 10 + Number of electrons in the valence shell = 10 + 8 = 18.

Period of the element = Number of principal quantum number of the valence shell = 5th.

Element E ($Z = 59$): Name of element = Praseodymium) (Pr

Electronic configuration of E: $1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2 5p^6\ 6s^2\ 5d^1\ 4f^2$.

But its actual electronic configuration is $6s^2$, $4f^3$.

The last electron enters into the 4*f*-orbital, therefore it belongs to *f-block elements*.

Group Number: Since it belongs to the lanthanide series therefore as such it does not have any group number of its own but it is considered to lie in group 3.

Period of elements: Number of principal quantum number of the valence shell = 6th.

Element F ($Z = 90$): Name of the element = Thorium (Th)

Electronic configuration of F: $[Rn]\ 6d^1 7s^2 5f^1$

But its actual electronic configuration is $[Rn]\ 6d^2 7s^2$.

The last electron enters into the 5f-orbital, therefore it belongs to f-block elements.

Group number: Since it belongs to actinide series, therefore as such it does not have any group number of its own but it is considered to lie in group 3.

Period of the elements = Number of principal quantum number of the valence shell = 7th.

II. **Elements A and B are representative elements** since their last electron enters in s- and p-orbitals respectively.

Element C is a transition element since its last electron enters in the d-orbital.

Element D is a p-block element with completely filled s- and p-orbitals of the valence shell and is called a noble gas.

Elements E and F are an inner transition elements since their last electron enters in the f-orbital.

ILLUSTRATION 1.11

Write the names and the atomic numbers (Z) of the following elements:

a. The fourth alkaline earth metal
b. The fifth alkali metal
c. The sixth element of the first transition series
d. The second inner transition elements and
e. The third noble gas

Sol.

a. Sr ($Z = 38$) b. Cs ($Z = 55$)
c. Fe ($Z = 26$) d. Pr ($Z = 59$)
e. Ar ($Z = 18$)

ILLUSTRATION 1.12

How do the electronic configuration of the elements with $Z = 106$–108 differ from one another?

Sol. Electronic configuration of $Z = 106 = 6d^4\,7s^2$

$$Z = 107 = 6d^5 7s^2$$
$$Z = 108 = 6d^6\,7s^2$$

Elements with $Z = 106$, has four, $Z = 107$, has five, while $Z = 108$ has six 6d-electrons.

ILLUSTRATION 1.13

Predict the name and position of the element in the periodic table with the electronic configuration $(n-1)d^8\,ns^2$ for $n = 5$.

Sol. For $n = 5$, the electronic configuration $= (5 - 1)d^8\,5s^2 = 4d^8 5s^2$. The element corresponding to this configuration is palladium (Pd) ($Z = 46$), which is a d-block element.

Group number = Number of electrons in $(n - 1)$ subshell + number of electrons in nth shell
$= 8 + 2 = 10$

Period of the elements: Number of principal quantum number of the valence shell = 5th.

ILLUSTRATION 1.14

Elements A to E have the following electronic configuration:

A: $[He]2s^2 2p^2$, B: $[Ne]3s^2 3p^2$, C: $[Ne]3s^2 3p^3$,
D: $[Ne]3s^2 3p^4$, E: $[Ar]4s^2$.

Which of the above will belong to the same group in the periodic table?

Sol. Elements having similar valence electronic configuration belong to the same group of the periodic table.

Therefore, elements A and B having four electrons in the valence shell, i.e. $2s^2$, $2p^2$ and $3s^2\,3p^2$ respectively belong to the same group, i.e. group 14 of the periodic table.

1.9 GENERAL INORGANIC CHEMISTRY OR PERIODIC TRENDS IN PROPERTIES OF ELEMENTS

The periodic law states that properties of the elements vary periodically with their atomic numbers. The basis of this periodicity lies in the periodic repetition of the electronic configuration of the elements as the atomic number increases. Regular variations in physical and chemical properties are observed down the group (↓) or along the period (→) in the periodic table. This regular gradation in properties is called **periodicity.**

For example, along the period (→), chemical reactivity tends to be high in group 1 metals, lower in elements towards the middle of the table, and increases to a maximum in the group 17 non-metals.

Similarly, down the group (↓) of representative metals (alkali and alkaline early metals) reactivity increases whereas down the group (↓) of non-metals (e.g. halogens) reactivity decreases.

1.9.1 Explanation of Periodicity

1. In a period from the left to the right there is a regular change in electronic configuration of elements.
2. In a group from the top to the bottom the outermost shell electronic configuration is similar.
3. The chemical properties of the element depend upon their electronic configuration. So, there is a regular change in chemical properties in a period and in a group, elements have similar chemical properties.

1.9.2 Trends in Physical Properties

There are various physical properties of elements which show periodic variation such as

1. Atomic and ionic radii
2. Screening or shielding effect
3. Penetration effect
4. Ionisation energy (IE or $\Delta_i H^\ominus$)
5. Electron gain enthalpy ($\Delta_{eg} H^\ominus$) and electron affinity (EA)
6. Electronegativity (EN) and its scales

7. Metallic and non-metallic properties
8. Polarity of covalent bond and percentage of ionic character
9. Bond strength
10. Acidic, basic and amphoteric character
11. Bond length
12. Bond angles
13. Periodicity of valence or oxidation stales
14. Typical elements
15. Bridge elements
16. Periodic trends and chemical reactivity
17. Magnetic properties
18. Fajans' rule (or change of ionic character to covalent character) or polarisability or polarisation
19. Inert pair effect
20. Factors which determine the formation (or stability) of the compounds
21. Lattice enthalpy ($\Delta_U H^{\ominus}$)
22. Hydration enthalpy ($\Delta_{hyd} H^{\ominus}$)
23. Flame colouration
24. Colour of substance in visible light
25. $p\pi$–$p\pi$ multiple bond
26. $p\pi$–$d\pi$ multiple bond
27. Hydrogen bonding
28. Geometry, shape and hybridisation of compounds and ions
29. Lanthanide and actinide contraction
30. Dipole moment

1.10 ATOMIC RADIUS

Determination of the size of an atom is very complicated and cannot be precise due to:

1. The size of an atom (~1.2 Å or 1.2×10^{-10}m in radius) is very small.
2. The electron cloud surrounding the atom does not have a sharp boundary.

There is no practical way by which the size of an individual atom can be measured. However, atomic size can be made by knowing the distance between the atoms in the combined state.

The distance from the centre of the nucleus to the outermost shell containing the electrons is called atomic radius. It is a very important property of an atom since different physical and chemical properties of atoms are related to it. It refers to both the covalent or metallic radii depending on whether the element is a non-metal or a metal.

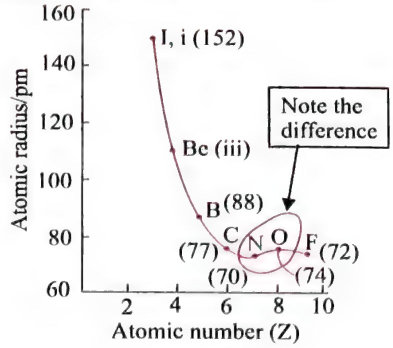


Fig. 1.4 (a) Variation of atomic radius with atomic number across the second period

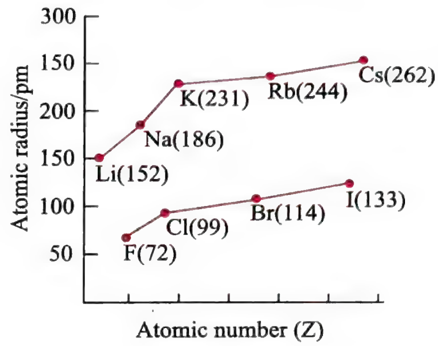


Fig. 1.4 (b) Variation of atomic radius with atomic number for alkali metals and halogens

Exceptions: Elements of 2nd and 3rd transition series (i.e. 4*d* a 5*d* series) belonging to the same vertical columns are similar size and properties because of the intervention of lanthanides shown in Fig. 1.4(c).

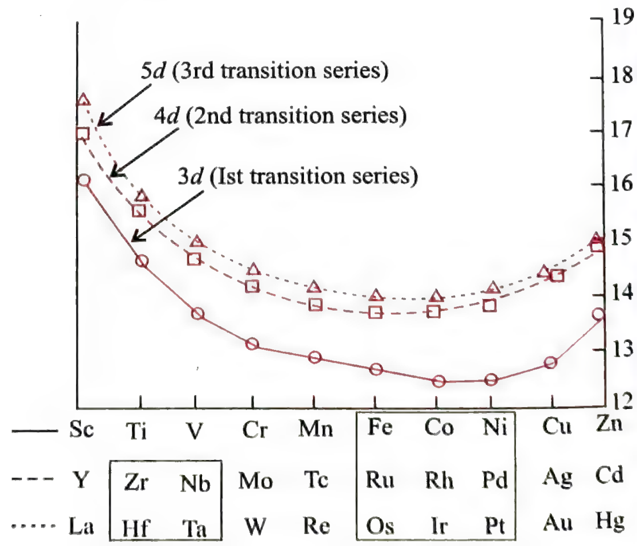


Fig. 1.4 (c) Trends in atomic radii of transition elements

1.10.1 Types of Atomic Radii

These are of four types:

1. **Covalent radius:** It is one-half of the distance between the nuclei (internuclear distance) of two covalently bonded like atoms in a homo-diatomic molecule which is called the covalent radius of that atom.

   $r_{covalent}$ or $r_c = \frac{1}{2}$ [bond length]

   For example, bond distance in Cl_2 molecule = 198 pm.

   r_{Cl} (covalent) = 198/2 = 99 pm.

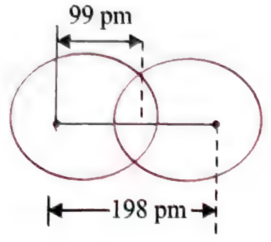


Fig. 1.5 Overlapping of atomic orbitals to form a covalent bond

   The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation.

2. **Metallic radius:** Metal atoms are assumed to be closely packed spheres, which are considered to touch one another in metallic crystal.

   Metallic radius is half the internuclear distance separating the metal cores in the metallic crystal. For example, the distance between the two adjacent copper atoms in solid copper is 256 pm; hence, the metallic radius of copper is 256/2 = 128pm.

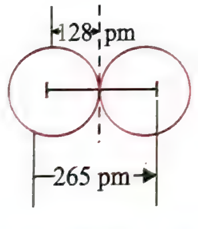


Fig. 1.6 No overlapping of atomic orbitals

Thus, metallic radius > covalent radius.

3. **van der Waals radius:** It represents the overall size of the atom which includes its valence shell in a non-bonded situation. It is half of the distance between two similar atoms in separate molecules in a solid.

Thus, van der Waals radius > metallic radius > covalent radius.

Covalent radius of two Cl atoms in Cl_2 molecule [Fig. 1.7 (a)], van der Waals radius of Cl atoms in two non-bonded isolated Cl atoms [Fig. 1.7 (b)] and covalent and van der Waals radii in two Cl_2 molecules [Fig. 1.8] are shown below.

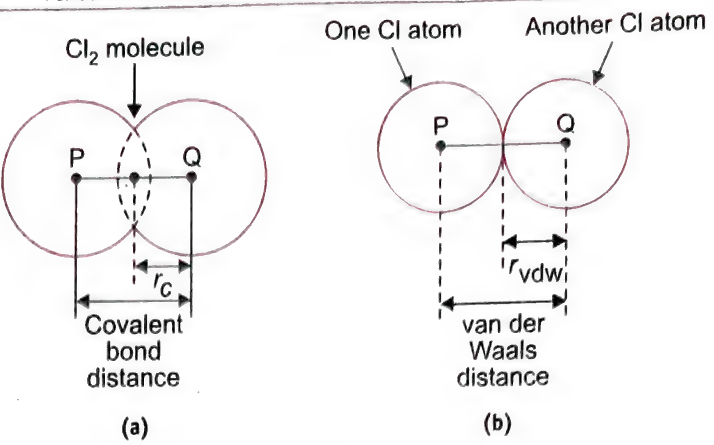


Fig. 1.7

In Fig. 1.7 (a), electron clouds of two Cl atoms merge with each other and $r_c = PQ/2$, while in Fig. 1.7 (b), two Cl atoms are just in contact with each other (no bond formation). Therefore $r_{vdw} = PQ/2$.

When two Cl_2 molecules formed by overlapping of electron clouds of two Cl atoms that are brought in close contact with each other (no bond formation) (Fig. 1.8). Then r_{vdw} of two Cl_2 molecules = $PS/2$ = 180 pm; and r_c of two Cl_2 molecules = $RS/2$ = 99 pm.

It may be noted that r_{vdw} of two atoms or of two Cl_2 molecules is greater than r_c of two atoms or molecules. This is because in the formation of covalent bond, atoms have to overlap each other while in the formation of bonds, atoms/molecules simply come closer to each other and do not enter overlapping (no bond formation).

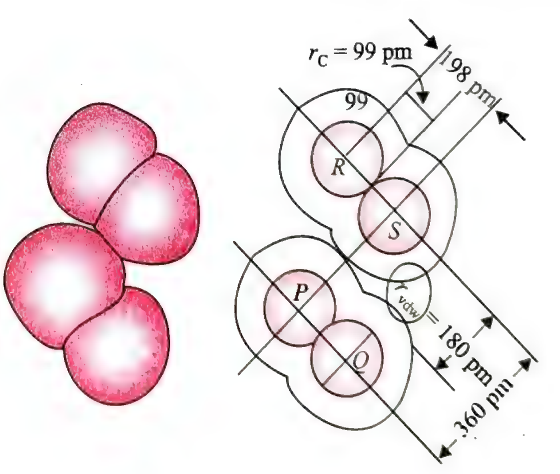
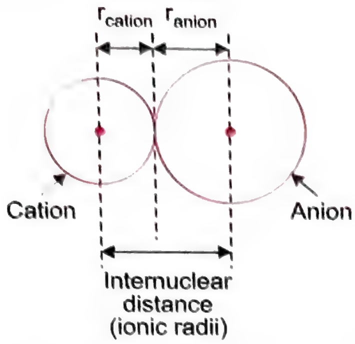


Fig. 1.8 Covalent and van der Waals radii in a chlorine molecule. The inner circles correspond to the size of the chlorine atom (r_{vdw} and r_c are van der Waals and covalent radii respectively).

4. **Ionic radii:** A neutral atom changes to a cation by the loss of one or more electrons and to an anion by the gain of one or more electrons. The number of charge on cation and anion is equal to the number of electrons lost or gained respectively. The ionic radii of the ions present in an ionic crystal may be calculated from the internuclear distance between the two ions.



The ionic radius is the distance between the nucleus of an ion and the point where the nucleus exerts its influence on the electron cloud.

The characteristics of ionic radii are as follows:

a. The ionic radius of a particular ion is of constant magnitude.

b. Ionic radii have an additive character, i.e. the inter nuclear distance between two ions is equal to the sum of the radii of the ions of which the ionic crystal is composed. Thus,

$r_{cation} + r_{anion} = r_{ionic\ radii}$

For example, $r_{Na^{\oplus}} = 95$ pm and the internuclear distance between the ion pairs in NaCl ionic crystal is 276 pm.

$\therefore r_{Cl^{\ominus}} + r_{Na^{\oplus}} = r_{ionic\ radii}$

$\therefore r_{Cl^{\ominus}} = r_{ionic\ radii} - r_{Na^{\oplus}}$

$= 276 - 95 = 181$ pm

i. Radius of cation: Radius of a cation is invariably smaller than that of the corresponding neutral atom

	Na	$Na^{\oplus}$
Number of electrons =	11	10
Number of protons (p's) =	11	11
	$1s^2, 2s^22p^6, 3s^1$	$1s^2, 2s^22p^6$

ii. Radius of an anion: Radius of an anion is invariably bigger than that of corresponding atom

	Cl	$Cl^{\ominus}$
Number of $e^{\ominus}$ =	17	18
Number of p =	17	17

iii. Isoelectronic species: A series of atom, ions and molecules in which each species contains same number of electrons but different nuclear charge is called isoelectronic species.

	N^{3-}	O^{2-}	$F^{\ominus}$	Ne	$Na^{\oplus}$	Mg^{2+}	Al^{3+}
Number of electrons	10	10	10	10	10	10	10
Number of protons	7	8	9	10	11	12	13
Ratio $\left(\frac{Z}{e^{-}}\right)$	0.7	0.8	0.9	1.0	1.1	1.2	1.3
Ionic radius(pm)	171	140	136	112	95	65	50

Note: Smaller the value of $\left(\frac{Z}{e^{-}}\right)$, larger the size of that species.

- Number of electrons is same.
- Number of protons is increasing.
- So, the effective nuclear charge is increasing and atomic size is decreasing. In an isoelectronic series atomic size decreases with the increase of charge. Some of the examples of isoelectronic series are as under.

$S^{2-}, Cl^{\ominus}, K^{\oplus}, Ca^{2+}, Sc^{3+}$

$SO_2, NO_3^{\ominus}, CO_3^{2-}$

N_2, CO, $CN^{\ominus}$

NH_3, $H_3O^{\oplus}$

1.10.2 Periodicity in Atomic Radius and Ionic Radius

1. For normal elements:

a. In a period from the left to the right the effective nuclear charge (Z_{eff}) increases because the next electron fills in the same shell. So, the atomic size decreases. For example the covalent radii of the second period elements in Å are as follows:

Li	Be	B	C	N	O	F
1.23	0.89	0.80	0.77	0.74	0.74	0.72

b. In a group moving from the top to the bottom the number of shells increases. So, the atomic size increases. Although the effective nuclear charge increases its effect is negligible in comparison to the effect of increasing number of shells. For example, the covalent radii of IA group elements in Å are as follows:

Li	Na	K	Rb	Cs
1.23	1.57	2.03	2.16	2.35

2. The atomic radius of the inert gas (zero group) is shown the largest in a period because of its van der Waals radius which is generally larger than the covalent radius. The van der Waals radius of inert gases also increases in moving from the top to the bottom in a group.

ILLUSTRATION 1.15

Which of the following species will have the largest and the smallest size Mg, Mg^{2+}, Al, Al^{3+}?

Sol. Atomic radii decrease along the period. Cations are smaller than their parent atoms. Among isoelectronic species the one with the larger positive nuclear charge will have a smaller radius.

The largest species is Mg; the smallest one is Al^{3+}.

$Mg > Al > Mg^{2+} > Al^{3+}$

ILLUSTRATION 1.16

a. Compare the size of Cl, $Cl^{\ominus}$ and Fe^{2+} ion.

b. The radii of Ar is greater than the radii of chlorine. Explain.

Sol.

a. $\frac{Z}{e^{-}}$ ratio for Cl $= \frac{17}{17} = 1.00$

$Cl^{\ominus} = \frac{17}{18} = 0.944$

$Fe^{2+} = \frac{26}{24} = 1.08$

$Cl^{\ominus} > Cl > Fe^{2+}$

b. **Explanation:** In chlorine, the radii mean the atomic or covalent radii which is actually half the intermolecular distance between two atoms, whereas in argon the radii mean the van der Waals radii as argon is not a diatomic molecule. van der Waals radii is actually half the distance between adjacent molecule. So, van der Waals radii being larger than the atomic radii. Hence, argon has a larger radii than chlorine.

ILLUSTRATION 1.17

a. Give and explain the decreasing order of atomic radius of fluorine (F), nitrogen (N) and oxygen (O).

b. Give the decreasing order of van der Waals radii: N, O, H, Cl, Br.

Sol.

a. Decreasing order of atomic radius is O > F > N.

Explanation: The atomic size generally decreases across a period as shown Fig. 1.4 (a) for the elements of the second period. Because within period the outer electrons are in the same valence shell and the effective nuclear charge (Z_{eff}) increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus.

So, the decreasing order of atomic radius should be N > O > F.

But it is not observed, since from N to O, Z_{eff} increases, so the size should decrease from N to O. But in oxygen pairing of electrons takes place, so due to the repulsion between paired electrons, size of O > N. [$N = 2s^2\,2p^3$, $O = 2s^2\,2p^4$]

Similarly, due to the repulsion between two lone pairs of electrons in F ($2s^2\,2p^5$), the size should increase from O to F. But high nuclear charge of F than that of O, compensates the repulsion between two pairs of electrons. Hence, size of O > F.

Thus decreasing order of atomic radius is O > F > N.

b. $r_{vdw} \propto$ Numbers of energy shells and

$$r_{vdw} \propto \frac{1}{\text{Nuclear charge}}$$

i. H has only one energy shell ($n = 1$), Cl has three ($n = 3$) and Br has four ($n = 4$). Therefore,

$$r_{vdw} \text{ of Br} > r_{vdw} \text{ of Cl} > r_{vdw} \text{ of H}$$

ii. Both N and O have two energy shells ($n = 2$), but Z on oxygen (+ 8) is greater than on N (+ 7). Therefore,

$$r_{vdw} \text{ of N} > r_{vdw} \text{ of O}$$

Hence, the decreasing order of r_{vdw} is

Br > Cl > N > O > H

ILLUSTRATION 1.18

a. In the sixth period, after filling of $6p$ orbitals, the next electron (i.e. 57th) enters the $5d$-orbital against aufbau principal and there after the filling of seven $4f$-orbitals starts with cerium ($Z = 58$) and ends up with lutetium ($Z = 71$). Explain this anomalous behaviour.

b. In the seventh period, after the filling of $7s$-orbital, the next two electrons (i.e. 89th and 90th) enter the $6d$-orbital against *Aufbau principle* and there after the filling of seven $5f$-orbitals begins with proactinium (Pr, $Z = 91$) and ends up with lawrencium (Lr, $Z = 103$). Explain this anomalous behaviour.

Sol.

a. This can be explained on the basis of greater stability of the xenon (inert gas) core. After barium (Ba, $Z = 56$), the addition of the next electron (i.e. 57th), should occur in $4f$-orbitals in accordance with *aufbau principle.* Since the $4f$-orbitals lie inside the core, and will tend to destatabilise the xenon core.

$Z = 54, \Rightarrow [Kr]4d^{10}4f^0\,5s^25p^65d^0$

Therefore, the 57th electron prefers to enter $5d$-orbitals which lies outside the xenon core and whose energy is only slightly greater than that of $4f$-orbitals.

Thus, stability of the atom due to xenon core compensates more than the slight instability caused by the addition of one electron to the higher energy $5d$-orbital instead of the lower energy $4f$-orbital.

Thus, the outer electronic configuration of La ($Z = 57$) is $5d^16s^2$ rather than the expected $4f^16s^2$. Once $5d$-orbital has one electron, the next electron (i.e. 58th) instead of entering the outer $5d$-orbital, enters the inner $4f$-orbital. This is due to greater nuclear charge and thereafter the continuous filling of the $4f$-sub shell occurs till it is complete at lutetium (Lu, $Z = 71$, $4f^{14}5d^16s^2$)

b. The anomalous behaviour is due to:

i. The smaller energy difference between $5f$- and $6d$-orbitals than between $4f$- and $5d$-orbitals.

ii. Due to the greater stability of radon (Rn, $Z = 86$), the next two electrons (i.e. 89th and 90th) after filling the $7s$-orbital prefer to enter $6d$-orbitals before filling of $5f$-orbitals begin with proactinium (Pa, $Z = 91$) and continues till it is complete with lawrencium (Lr, $Z = 103$).

ILLUSTRATION 1.19

Which of the following species are isoelectronic?

i. Ne	**ii.** O^{2-}	**iii.** Mg^{2+}	**iv.** F
v. Al^{3+}	**vi.** $Cl^{\ominus}$	**vii.** K	**viii.** Na

Arrange them in decreasing order of their size.

Sol. The number of electrons in these species are:

i. Ne = 10 **ii.** $O^{2-} = 8 + 2 = 10$

iii. $Mg^{2+} = 12 - 2 = 10$ iv. $F = 9$

v. $Al^{3+} = 13 - 3 = 10$ vi. $Cl^{\ominus} = 17 + 1 = 18$

vii. $K = 19$ viii. $Na = 11$

Thus Ne, O^{2-}, Mg^{2+}, Al^{3+} are isoelectronic species (each one of which has 10 electrons).

Nuclear charge on these isoelectronic species are as:

$Ne = +10$ $O^{2-} = +8$

$Mg^{2+} = 12$ $Al^{3+} = 13$.

Size of the species decreases as the nuclear charge increases, therefore the size of isoelectronic species decreases in the order.

$O^{2-} > Ne > Mg^{2+} > Al^{3+}$.

ILLUSTRATION 1.20

Which of the following species has the smallest size?

a. $K^{\oplus}$, Sr^{2+}, Ar b. Si, P, Cl c. O, $O^{\ominus}$, O^{2-}

Sol.

a. Z for Sr^{2+}, $K^{\oplus}$ and Ar = 38, 19 and 18 respectively.

Electronic configuration of Sr = [Kr] $5s^2$

Electronic configuration of Sr^{2+} = [Kr] (it has four shells)

Electronic configuration of K = [Ar]$4s^1$

Electronic configuration of $K^{\oplus}$ = [Ar] (it has three shells)

Ionic size of Sr^{2+} is smaller than that of $K^{\oplus}$, due to higher nuclear charge which compensates the effect of additional shell.

Since $K^{\oplus}$ and Ar are isoelectronic species with 18 electron each. So, $\frac{Z}{e^-}$ for $K^{\oplus} = \frac{19}{18} = 1.05$ and $\frac{Z}{e^-}$ for $Ar = \frac{18}{18} = 1.0$.

Smaller is the value of $\frac{Z}{e^-}$, larger the size of that species.

So decreasing order of size is

$Ar < K^{\oplus} < Sr^{2+}$

b. Z for Si, P and Cl = 14, 15, 17

Decreasing order of size is

Si > P > Cl

Thus, Cl is of the smallest size.

Moreover, along the period, size decreases from the left to the right. All of then belong to the 3rd period.

c. Species with more negative charge is larger than its parent atom.

Thus, the decreasing order of size is

$O^{2-} > O^{\ominus} > O$.

Thus, O is the smallest in size.

ILLUSTRATION 1.21

Arrange the following in order of decreasing radii?

a. $F^{\ominus}$, O^{2-}, N^{3-}, S^{2-} b. P, Si, N, C, c. $I^{\ominus}$, $I^{\oplus}$, I

Sol.

a. Since $F^{\ominus}$, N^{3-}, O^{2-} are isoelectronic species (with 10 electrons). So, size of anions decreases as nuclear charge increases (Z for $F^{\ominus}$, O^{2-}, N^{3-} = 9, 8 and 7 respectively)

So, decreasing order of size among isoelectronic anions are as:

$N^{3-} > O^{2-} > F^{\ominus}$

Since S belongs to the 3rd period while F, O, N all belong to the 2nd period. Therefore, size of S^{2-} is largest.

Thus overall order of decreasing size is

$S^{2-} > N^{3-} > O^{2-} > F^{\ominus}$

b. C and N belong to the 2nd period whereas Si and P belong to the 3rd period. Elements in the 3rd period have higher atomic sizes than those of the 2nd period due to increase in shells. Thus, size of Si and P are higher than those of C and N respectively.

Moreover, along the period atomic sizes decrease from the left to the right due to the increased nuclear charge. Thus, size of C > N and Si > P. Thus, overall decreasing order of atomic sizes is

Si > P > C > N

c. Decreasing order of radii is

$I^{\ominus} > I > I^{\oplus}$

because the size of anion is always greater while that of an cation is always smaller than the parent atom.

1.11 SCREENING OR SHIELDING EFFECT OF INNER SHELL ELECTRONS ON THE VALENCE SHELL ELECTRON

In multi-electron atoms, the valence shell electrons are attracted by the nucleus and repelled by the electrons in the inner shell. The combined effect of these two opposing forces is that the attractive force exerted by the nucleus on the valence shell electrons is partially decreased or weakened by the repulsive force exerted by the electrons present in the inner shell. Thus, the valence shell electrons experience less charge of the nucleus.

The actual charge experienced by the valence shell electrons is called *effective nuclear charge* and the repulsive force experienced by the valence shell electrons from the electrons present in the inner shells is called the *shielding or screening* effect. Thus, the effective nuclear charge (Z_{eff}) is

Z_{eff} = Total nuclear charge (Z) – Screening constant (σ)

1.11.1 Factors Affecting the Magnitude of Screening Effect

Number of inner shells: σ depends on the numbers of electrons in the inner shells. The greater the number of inner electrons, large is the screening effect and hence larger is the magnitude of σ and hence the magnitude of Z_{eff} will decrease.

As the screening effect increases, Z_{eff} decreases. Consequently the force of attraction by the nucleus for the valence shell electrons decreases and hence the ionisation enthalpy decreases down the group (↓).

1.11.2 Calculation of σ and Z_{eff} by Slater's Rule

The magnitude of 'σ' and hence that of 'Z_{eff}' can be calculated by using Slater's rule, as follows.

1. **For *ns*- or *np*-orbital electrons:**
   a. Write the electronic configuration of the element in the following order and group them as
   (1*s*), (2*s*, 2*p*), (3*s*, 3*p*), (3*d*), (4*s*, 4*p*), (4*d*, 4*f*), (5*s*, 5*p*), (5*d*, 5*f*), (6*s*, 6*p*), etc.
   b. Electrons to the right of the (*ns*, *np*) group are not effective in shielding the *ns* or *np* electrons and contribute nothing to σ.
   c. All other electrons in the (*ns*, *np*) group contribute to the extent of 0.35 each to the screening constant (except for 1*s* for which the value is 0.30).
   d. All the electrons in the $(n-1)$th shell contribute 0.85 each to the screening constant.
   e. All the electrons in the $(n-2)$th shell or lower contribute 1.0 each to the screening constant.
2. **For *d*- or *f*-electrons:** Rules (a) to (c) remain same but rules (d) and (e) get replaced by rule (f).
   f. All the electrons in the groups lying left to (*nd*, *nf*) group contribute 1.0 each to the screening effect.

ILLUSTRATION 1.22

Calculate the effective nuclear charge experienced by the 4*s*-electron in potassium atom ($Z = 19$).

Sol. The electronic configuration of K is $1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6, 4s^1$, and this atom has 4 shells in it. Therefore,

$$(Z_{\text{eff}})_{4s} = Z - \sigma$$

$$\therefore \quad \sigma = \begin{pmatrix} 0.85 \times \text{Number of electrons in } (n-1)\text{th} \\ \text{shell} + 1.00 \times \text{ Total number of electrons} \\ \text{in the inner shell} \end{pmatrix}$$

$$= 0.85 \times 8 + 1.00 \times 10$$
$$= 16.80$$

Hence, $Z_{\text{eff}} = Z - \sigma = 19 - 16.80 = 2.20$

ILLUSTRATION 1.23

Calculate the effective nuclear charge of the last electron in an atom. The electronic configuration is $1s^2, 2s^2 2p^6, 3s^2 3p^5$.

Sol. $Z = 2 + 2 + 6 + 2 + 5 = 17$. and this atom has 3 shells in all.

$$\therefore \quad \sigma = \begin{bmatrix} 0.35 \times \text{Number of electrons left} \\ \text{in } n\text{th shell} + (0.85 \times \text{ Number of} \\ \text{electrons in } (n-1)\text{th shell} + (1.00 \times \\ \text{Total number of electrons in the} \\ \text{inner shells)}) \end{bmatrix}$$

$$= (0.35 \times 6) + (0.85 \times 8) + (1 \times 2)$$
$$= 10.9$$

Thus, $Z_{\text{eff}} = (Z - \sigma) = 17 - 10.9 = 6.1$

ILLUSTRATION 1.24

Calculate the screening constant in Zn.

a. For a 4*s*-electron **b.** For a 3*d*-electron

Sol. The electronic configuration of Zn ($Z = 30$) is $1s^2; 2s^2 2p^6; 3s^2\, 3p^6; 3d^{10}; 4s^2$.

Since σ is calculated for one electron in 4*s* shell, so one electron is left in 4*s* shell.

$$\textbf{a. } \sigma = \begin{bmatrix} (0.35 \times \text{Number of electrons left in } 4s \text{ or} \\ n\text{th shell}) + (0.85 \times \text{Number of electrons in} \\ (n-1)\text{th shell}) + (1.00 \times \text{Total number of} \\ \text{electrons in the inner shell}) \end{bmatrix}$$

$$= (0.35 \times 1) + (0.85 \times 18) + (1.00 \times 10)$$
$$= 25.65$$

b. i. σ for $4s = 0$, [Rule (b)]. (σ for right of (*ns*, *np*) is zero).

ii. Since σ is calculated for one electron in 3*d*-orbital, so, 9 electrons are left in 3*d*-orbital.

$$\therefore \sigma = \begin{bmatrix} \begin{pmatrix} 0.35 \times \text{Number of electrons left in} \\ 3d \text{ shell or } n\text{th shell} \end{pmatrix} \\ + \begin{pmatrix} 1.00 \times \text{Number of electrons in the} \\ \text{inner shell} \end{pmatrix} \end{bmatrix}$$

$$= (0.35 \times 9) + (1.0 \times 18)$$
$$= 21.15$$

3. **Type of orbitals occupied by the electrons:**
   a. Due to different shapes and orientation of different orbitals, the screening power decreases as follows:

$$\xrightarrow[\text{Sereening power decreases}]{ns > np > nd > nf}$$

   From the shapes of electron charge clouds of orbitals, it is clear that the *ns*-orbitals are spherical symmetrical in shape. Therefore, it screens the nuclear charge more effectively than *np*-orbitals which are dumbell in shape. Similarly, *np*-orbitals screen the nuclear charge more effectively than *nd*-orbitals which double dumbell in shape which in turn screens the nuclear charge much more effectively than *nf*-orbitals which are diffused and complex in shape and orientation.

   This order also means that the electrons present in *d*- and *f*-orbitals are much more shielded than those in *s*- or *p*-orbitals by the inner shell electrons. Thus an electron in *np*-orbital is more effectively shielded than the *ns*-electron by the inner shell electrons.

   For example, consider Be ($1s^2\, 2s^2$) and B ($1s^2\, 2s^2 2p^1$) atoms, 2*p* electrons of B atom are more effectively shielded by 1*s* and 2*s* electrons while the 2*s* electrons of Be atom are not effectively shielded by the 1*s* electrons and second 2*s* electron.

   b. An electron present in the *n*th orbital is more effectively shielded by the electrons in the $(n-1)$th orbital while the same electron is not effectively shielded by the other electron present in the same orbital.

   For example, in Li atom ($1s^2\, 2s^1$); $2s^1$ electron is more effectively shielded by two electrons present in 1*s*-orbital while in He atom ($1s^2$) one of the two electrons in 1*s*-orbital is not effectively screened by

the other electron present in the same orbital i.e., 1*s*-orbital.

c. Application of shielding effect:

i. This concept has been used to explain why the ionisation potential values of the elements of a given group decreases down the group (↓).

ii. It has been used to explain why a large decrease in the value of ionisation potential is observed when we proceed from an inert gas to alkali metals.

iii. It has been used in explaining the inert pair effect.

iv. It has been used to explain the lanthanide and actinide contraction.

4. Variation of screening effect or σ in the periodic table: Greater is the magnitude of σ, greater is the amount of shielding effect caused by the intervening electrons on the valence shell electrons.

Since σ increases both down the group (↓) of and along the period (→), so the magnitude of screening effect also increases in the same direction.

s-block elements		*p*-block elements					
1	2	13	14	15	16	17	18

σ or shielding effect ——→ Increases

↓

Increases

5. Variation of effective nuclear charge in the periodic table:

a. It is observed that the magnitude of effective nuclear charge or effective atomic number increases in a period when we move from the left to the right.

IInd period	Li	Be	B	C	N	O	F	Ne
Z	3	4	5	6	7	8	9	10
σ	1.7	2.05	2.40	2.75	3.10	3.45	3.80	4.15
Z_{eff} = (Z – σ)	1.3	1.95	2.60	3.25	3.90	4.55	5.20	5.85

b. In the subgroup of normal elements the magnitude of effective atomic number remains almost the same, as shown below:

Ist group	Li	Na	K	Rb	Cs
Z	3	11	19	37	55
σ	1.7	8.8	16.8	34.8	52.8
Z_{eff} = (Z – σ)	1.3	2.2	2.2	2.2	2.2
2nd group	Be	Mg	Ca	Sr	Ba
Z	4	12	20	38	56
σ	2.05	9.15	17.15	35.15	53.15
Z_{eff} = (Z – σ)	1.95	2.85	2.85	2.85	2.85

s-Block elements		*p*-Block elements					
1	2	13	14	15	16	17	18

Effective nuclear charge (Z_{eff}) ——→ Increasses

↓

Remains almost the same

6. Application of effective nuclear charge: On the basis of Z_{eff}, the following facts can be explained:

a. A cation is smaller in size than its parent atom.

b. An anion is larger in size than its parent atom.

c. The order of successive ionisation potential IP_1, IP_2, IP_3 ... etc. of an atom is in the following order:

$IP_1 < IP_2 < IP_3$

d. *Why 4s-orbital is filled before 3d-orbitals:* The lower the values of Z_{eff} acting on the 3*d*-electron as compared to on 4*s*-electrons, shows that 3*d* electron is less tightly bound to the nucleus than the 4*s*-electron.

Consequently, the additional electron in atom prefers to enter 4*s*-orbital than 3*d*-orbital.

For example, let the two electronic configuration of potassium (K, Z = 19), are as shown below:

i. $1s^2, 2s^2\,2p^6; 3s^2\,3p^6\,3d^0; 4s^1$ $\left(\begin{array}{l}\text{4s-orbital is filled}\\ \text{before 3d orbitals}\end{array}\right)$

ii. $1s^2, 2s^2 2p^6; 3s^2\,3p^6\,3d^1; 4s^0$ $\left(\begin{array}{l}\text{3 d-orbital is filled}\\ \text{before 4s-orbital}\end{array}\right)$

Therefore, σ on 4*s*-electron as calculated by Slater rule is

$$(\sigma)_{4s^1} = \begin{bmatrix}(0.85 \times \text{No. of electrons in } (n-1)\text{th shell})\\ +1.00 \times \text{No. of electrons in the inner shell}\end{bmatrix}$$

$$= (0.85 \times 8) + (1.00 \times 10) = 16.8$$

$$\therefore \quad Z_{eff} = Z - \sigma = 19 - 16.8 = 2.20$$

Similarly, σ on 3*d*-electron is

$$(\sigma)_{3d^1} = [1.00 \times \text{Total no. of inner electrons}]$$

$$= (1.00 \times 18) = 18$$

$$\therefore Z_{eff} = Z - \sigma = 19 - 18 = 1$$

Hence, Z_{eff} of 3*d*-electron is less than that of 4*s*-electron. So, additional electron in potassium (K) atom prefers to enter 4*s*-orbital than 3*d*-orbital.

e. *Why 4s-electrons are removed before 3d-electrons in the conversion of 3d-transition elements into cations:*

The greater the value of Z_{eff} on one of the 3*d*-electrons than 4*s*-electrons in an atom shows that 3*d*-electrons are more tightly held to the nucleus than the 4*s*-electrons. Consequently, in the conversion of atom into cations the electrons to be removed are 4*s*-electrons and not 3*d*-electrons.

For example, consider the conversion of vanadium atom (V; $Z = 23$) into V^{+2} cation and V^{+2} is formed by the removal of two electrons from 4*s*-orbitals and not from 3*d*-orbital. Thus,

$V(1s^2, 2s^2\ 2p^6;\ 3s^2 3p^6,\ 3d^3,\ 4s^2) \rightarrow V^{+2}\ (1s^2;\ 2s^2 2p^6;\ 3s^2 3p^6 3d^3) + 2e^-$

Calculation Z_{eff} on of the 4*s*-electron is given by:

$$(\sigma)_{4s^1} = \begin{bmatrix} (0.35 \times \text{No. of electrons left in the } n\text{th shell}) \\ + (0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) \\ + (1.00 \times \text{No. of electrons in the inner shell}) \end{bmatrix}$$

$$= (0.35 \times 1) + (0.85 \times 11) + (1.00 \times 10) = 19.70$$

$$Z_{eff} = Z - \sigma = 23 - 19.70 = 3.30$$

Calculation of Z_{eff} on one of the 3*d*-electron is given by:

$$(\sigma)_{3d^1} = \begin{bmatrix} (0.35 \times \text{No. of electrons left in the} \\ 3d\text{-orbitals}) + (1.00 \times \text{Total no. of} \\ \text{electrons in the inner orbitals}) \end{bmatrix}$$

$$= (0.35 \times 2) + (1 \times 18) = 18.70$$

$$Z_{eff} = Z - \sigma = 23 - 18.70 = 4.30$$

Hence, Z_{eff} of one of the 3*d*-electrons is greater than 4*s*- electrons in vanadium atom shows that 3*d*-electrons are more strongly held to the nucleus than the 4*s*-electrons. Consequently in the conversion of $V \rightarrow V^{+2}$, 4*s*-electrons are removed and not 3*d*-electrons.

CONCEPT APPLICATION EXERCISE 1.1

1. 3*d*-, 4*d*- and 5*d*-series consists of 10 elements each? Explain.
2. Why the *f*-block elements are called inner transition element?
3. Transition elements show horizontal as well as vertical relationship. Explain.
4. Be and Al are placed in different periods and groups but they show the similar properties. Explain.
5. The outer electronic configuration of some elements are given below:

   a. $6d^1\ 7s^2$ **b.** $4f^1\ 5d^1\ 6s^1$

   c. $2s^2\ 2p^6\ 3s^2$ **d.** $3d^5\ 4s^1$

   e. $4s^2, 4p^3$

   State to which of the periodic table each of these elements belongs.
6. Arrange the following elements in decreasing order of metallic character:
   K, Mg, B, Al.
7. Name the species that will be isoelectronic with the following atoms or ions.

   a. Ca^{2+} **b.** Ne

   c. $Cl^{\ominus}$ **d.** $Rb^{\oplus}$
8. Which one of the following pairs would have a smaller size. Explain.

   a. $Na^{\oplus}$ or Mg^{2+} **b.** O^{2-} or $F^{\ominus}$

   c. P or As
9. Arrange the following ions in order of their decreasing ionic radii.
   $Li^{\oplus}, K^{\oplus}, Mg^{2+}, Al^{3+}$
10. What property did Mendeleev use to classify the elements in his periodic table.
11. Elements with $Z = 107$, 108 and 109 have been made recently. Indicate the groups to which they belong.
12. Why Zn, Cd and Hg are not considered as typical transition elements?
13. Why Cu, Ag and Au are transition elements, although they have completely filled *d*-orbitals?
14. Half-filled and full-filled orbitals are stable. Why?
15. What are super heavy elements?
16. How many anomalous pairs were present in original Mendeleev periodic table?
17. How many *s*-block elements are known?
18. Which block of elements consists of metals, non metals and metalloids?
19. Which is the hardest elements?
20. Which elements is lowest melting point liquid metal?
21. Which element is heaviest melting and boiling point metal?
22. Name the liquid non-metal.
23. Name the best and the poorest conductor of current among metals.
24. Name the heaviest solid metal.
25. Name the most poisonous element.
26. Name the heaviest naturally occurring element.
27. Among the radioactive elements, which is a liquid element?
28. Name the element having the lowest electronegative, lightest and liquid metal.
29. Name the lightest solid non-metal having the highest tensile strength.
30. Which element has highest catenation property?
31. Which non-metal sublime on heating and have metallic lusture.
32. Which is the most stable element?
33. Name the element which is the poorest conductor of current among non-metals.
34. Name the elements with highest EN and with highest EA or $\Delta_{eg}H^{\ominus}$.
35. Which element is used in the making of high temperature thermometer?
36. Which element is used in the making of infrared (IR) windows, prisms and lenses?

37. Answer the following:
   a. Name the element not known at the time of Mendeleev.
   b. Name any two typical elements.
   c. Name any two bridge elements.
   d. Name two pairs showing diagonal relationship.
   e. Name two transition elements.
   f. Name two rare earth elements.
   g. Name two transuranic elements.
   h. In which case compounds of Cr show maximum radius.
      i. K_2CrO_7 **ii.** CrO_2Cl_2
      iii. $Cr_2(SO_4)_3$ **iv.** $CrCl_2$

38. In *s*- and *p*-block elements the OS. changes by 2 units, but in transition elements it changes in units of one. Explain?

39. Mn_2O_7 is an acidic oxide, why?

40. Why Ar (argon) (at. wt. = 39.94) has been placed before K (at. wt. = 39.10) in the periodic table?

41. Why Ag is a noble metal and K is a highly reactive metal?

42. Calculate the screening constants of alkali metals for valency electrons.

43. Calculate the screening constants of members of the 2nd period for valency electrons.

ANSWERS

8. a. Mg^{2+} **b.** $F^{\ominus}$ **c.** P
9. $K^{\oplus} > Mg^{2+} > Al^{3+} > Li^{\oplus}$
10. Atomic masses
11. 7, 8 and 9 groups respectively
15. $Z > 100$
16. Four (Ar, K), (Co, Ni), (Te, I) and (Th, Pa)
17. Thirteen **18.** *p*-block
19. Carbon (diamond) **20.** Hg **21.** Tungsten (W)
22. Br **23.** Ag and Pb **24.** Os **25.** Pu
26. U **27.** Fr **28.** Cs **29.** B **30.** C
31. I **32.** Te **33.** S **34.** F and Cl respectively
35. Ga **36.** Ge

1.12 PENETRATION EFFECT OF ELECTRONS IN DIFFERENT ORBITALS

Due to different shapes and orientation of different orbitals, the penetration effect decreases as follows:

$$\xrightarrow[\text{penetration effect decreases}]{ns > np > nd > nf}$$

From the shapes of electron charge clouds of orbitals, it is clear that *ns*-orbitals are spherical symmetrical, therefore the electrons of *ns*-orbital has the maximum probability of being found near the nucleus and this probability goes on decreasing in case of *p*-, *d*-, and *f*-orbitals of the same shell.

In other words, *ns*-orbitals are spherical symmetrical in shape, therefore they are much more penetrated or attracted towards the nucleus than *np*-orbitals which are dumbell in shape. Similarly, *np*-orbitals are much more penetrated towards the nucleus than *nd*-orbitals which are double dumbell in shape, which in turn are more effectively penetrated towards the nucleus than *nf*-orbitals which are diffused and complex in shape and orientation.

1.12.1 Applications of Penetration Effect

1. If penetration effect of the electron is more, it will be closer to the nucleus and hence will be held more strongly by the nucleus. Consequently, the ionisation potential/energy will be high.

   Ionisation energy increases with the increase in the penetration effect of electrons in different orbitals.

2. Thus, the ionisation energy will be more to remove an electron from *ns*-orbital than an electron from *np*-orbital, which in turn, will be more than that required to remove an electron from *nd*-orbitals and so on.

3. For example, the first ionisation enthalpy of B < Be and Al < Mg.

   According to the general trend ionisation enthalpy increases along the period (→). But the observed order is found to be reverse, which can be explained by the penetration effect as below:

   Boron (B; $Z = 5$); $1s^2\ 2s^2 2p^1$

   Beryllium (Be, $Z = 4$); $1s^2\ 2s^2$

   In case of boron, an electron has to be removed from 2*p*-orbital to form $B^{\oplus}$-ion. Whereas in case of Be, an electron has to be removed from 2*s*-orbital to produce $Be^{\oplus}$-ion. Since 2*s*-orbital is much more penetrated towards the nucleus than 2*p*-orbital, hence the 2*p*-electrons of B is more shielded from the nucleus by the inner core of electrons than the 2*s*-electrons of Be. Therefore, it is easier to remove an electron from 2*p*-orbital than 2*s*-orbital of the same shell.

   Therefore, the first ionisation enthalpy of B is lower than that of Be.

   Similarly, the first ionisation enthalpy Al(Z = 13) ($1s^2$, $2s^2\ 2p^6$; $3s^2 3p^1$) is lower than that of Mg (Z = 12) ($1s^2$, $2s^2\ 2p^6$;$3s^2$).

1.13 IONISATION ENERGY/ENTHALPY (IE OR E_o) AND IONISATION POTENTIAL (IP)

1. Ionisation energy/enthalpy of an element is defined as the minimum amount of energy required to remove the outermost shell electron from an isolated gaseous atom (X) to form gaseous ion. It is usually represented as $\Delta_i H^{\ominus}$, or IE_1. For example,

   $X_{(g)} \longrightarrow X^{\oplus}_{(g)} + e^-$

2. Ionisation enthalpy is also known as ionisation potential (IP) since it is the minimum potential difference (in a discharge tube) required to remove the outermost electrons from an isolated gaseous atom to form gaseous ion.

3. Difference between ionisation energy (E_o or $\Delta_i H^{\ominus}$) and ionisation enthalpy ($\Delta_i H^{\ominus}$):

   Ionisation energy is defined as absolute zero, whereas at any other temperature it is defined as ionisation enthalpy and

in that case heat capacities for the reactants and products have to be taken into account. For example, enthalpies of reactions at any temperature (T) is:

$$X_{(g)} \longrightarrow X^{\oplus}_{(g)} + e^-$$

$$\Delta_r H^{\ominus}(T) = \Delta_r H^{\ominus}(O) + \int_0^T \Delta_r C_p^{\ominus} dT$$

The value of C_p for each species in the above equation is

$$\frac{5}{2}R\left(C_V = \frac{3}{2}R\right)$$

So, $\Delta_r C_p^{\ominus} = \frac{+5}{2}R$ (for ionisation).

Therefore,

$\Delta_r H^{\ominus}$ (ionisation enthalpy) = E_o (ionisation energy) + $\frac{5}{2}$ RT.

4. Units of IE and IP: It is measured in electron volts per atom (eV atom^{-1}) or kilo calories per mole (kcal mole^{-1}) or kilo joules per mole (kJ mole^{-1}). These quantities are related as:

Note: One electron volt is the energy acquired by an electron while moving under a potential difference of one volt.

$$\begin{aligned}
(1\text{eV atom}^{-1}) &= 3.83 \times 10^{-20} \text{ cal atom}^{-1} \\
&= 1.602 \times 10^{-19} \text{J atom}^{-1} \ (1 \text{ cal} = 4.184 \text{ J}) \\
&= 3.83 \times 10^{-20} \times 6.022 \times 10^{23} \text{ cal mol}^{-1} \\
&= 23.06 \times 10^3 \text{cal mol}^{-1} \\
&= 23.06 \text{ k cal mol}^{-1} \\
&= 1.602 \times 10^{-19} \times 6.022 \times 10^{23} \text{J mol}^{-1} \\
&= 96.49 \text{ kJ mol}^{-1}
\end{aligned}$$

Energy is required to remove electrons from an atom and hence ionisation enthalpies are always positive.

Ionisation enthalpy of hydrogen atom is 13.58 eV mol^{-1} or 13.58 × 96.49 = 1310.334 kJ mol^{-1}.

1.13.1 Successive Ionisation Enthalpies ($\Delta_i H^{\ominus}$ or IE)

The ionisation enthalpies to remove first, second, third etc. electrons from an isolated gaseous atom are called successive ionisation enthalpies. It is found that $\Delta_i H_2^{\ominus} > \Delta_i H_1^{\ominus}$ and $\Delta_i H_3^{\ominus} > \Delta_i H_2^{\ominus}$ and so on, i.e. $\Delta_i H_1^{\ominus} < \Delta_i H_2^{\ominus} < \Delta_i H_3^{\ominus}$ or $IE_1 < IE_2 < IE_3$....

Explanation: The second ionisation enthalpy will be greater than the first ionisation enthalpy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom.

In the same way the third ionisation enthalpy will be greater than the second and so on.

The term 'ionisation enthalpy', if not mentioned, is taken as the first ionisation enthalpy.

1.13.2 Factors Affecting the Magnitude of Ionisation Enthalpy

It depends on the following factors:

1. **Size of atom:** The values of ionisation potential of an element decreases (less positive value) as the atomic size increases.

$$\Delta_i H^{\ominus} \text{ or IE} \propto \frac{1}{\text{Atomic radius}}$$

In a larger atom, the outer electrons are far away from the nucleus and thus the force of attraction with which they are attracted by the nucleus is less and hence can be easily removed, so less IE.

For example, IE decreases down the group (↓) as shown in Table 1.9

Table 1.9 First IE of alkali metals in kJ mol^{-1}

Element	Li	Na	K	Rb	Cs
IE (kJ mol^{-1})	520	496	419	403	374

2. **Effective nuclear charge (Z_{eff}):** The greater the Z_{eff} on the nucleus of an atom, the more difficult it would be to remove an electron from the atom.

$$\Delta_i H^{\ominus} \text{ (or) IE} \propto Z_{eff}$$

With the increase in Z_{eff}, the electrons of the outer shell are more strongly held by the nucleus and hence greater energy is required to remove an electron from the atom.

For example, IE increases along the period (→) due to the increased Z_{eff} as shown in Table 1.10.

Table 1.10 First IE of second period elements in kJ mol^{-1}

Element	Li	Be	B	C	N	O	F	Ne
Nuclear charge (Z)	+3	+4	+5	+6	+7	+8	+9	+10
Z_{eff}	1.30	1.95	2.60	3.25	3.90	4.55	5.20	5.85
IE (kJ mol^{-1})	520	899	801	1086	1402	1314	1681	2080

Note the trends

3. **Shielding or screening effect of the inner shell electrons** (refer to Section 1.11): The shielding or screening effect increases if the number of electrons in the inner shells between the nucleus and the outermost electrons increases.

The screening effect reduces the force of attraction between the outermost electrons and the nucleus, hence the outermost electrons can be easily removed. Hence the value of IE decreases with the increase in screening effect.

$$\Delta_i H^{\ominus} \text{(or) IE} \propto \frac{1}{\text{Screening effect}}$$

4. **Penetration effect of orbitals** (refer to Section 1.12): Ionisation enthalpy increases as the penetration effect of the electrons in different orbitals increases. The order of energy required to remove electrons from s-, p-, d- and f-orbitals within the same shell is $s > p > d > f$.

Since s-orbital is more close to the nucleus and thus is more penetrated (or attracted) towards nucleus than the p-orbital of the same shell. Thus, it is easier to remove an electron from a p-orbital in comparison to s-orbital.

Generally the IE increases along the period (→).

Down the group (↓)

(With exception from Be to B and Mg to Al and N to O and P to S.)

Generally the IE decreases down the group (↓) with some exception in transition elements.

Application: First IE of B and Al should be greater than Be and Mg respectively. But the first IE of Be > B and Mg > Al. This is occurred due to the penetration effect of orbitals (*refer to Section* 1.12).

5. **Stability of half-filled and fully filled orbitals:** According to Hund's rule the stability of half-filled and completely filled degenerate orbitals has extra stability. Therefore, the removal of an electron from such an atom requires more energy than expected. For example,

a. IE_1 of Be $(Z=4\ (1s^2\ 2s^2)) >$ B $(Z=5)\ (1s^2\ 2s^2\ 2p^1)$, because Be has fully filled orbitals which is a stable electronic configuration.

b. Similarly, IE_1 of Mg $(Z = 12)(1s^2\ 2s^2\ 2p^6\ 3s^2) >$ Al $(Z=13)\ (1s^2\ 2s^2\ 2p^6\ 3s^2 3p_x^{\ 1})$

c. i. IE_1 of N $(Z=7)\ (1s^2\ 2s^2 2p_x^1 2p_y^1 2p_z^1) >$ O $(Z=8)\ (1s^2\ 2s^2 2p_x^2 2p_y^1 2p_z^1)$

Because N contains exactly half-filled *p*-orbitals which imparts greater stability to N, so removal of electron from N is difficult and hence IE_1 is high.

ii. Electronic configuration of O

$(Z=8)\ (1s^2\ 2s^2 2p_x^{\ 2}\ 2p_y^{\ 1}\ 2p_z^{\ 1})$

Electronic configuration of $O^{\oplus}$

$(Z=8)\ (1s^2\ 2s^2 2p_x^{\ 1}\ 2p_y^{\ 1} 2p_z^{\ 1})$

Electronic configuration of N

$(Z=7)\ (1s^2\ 2s^2\ 2p_x^{\ 1} 2p_y^{\ 1}\ 2p_z^{\ 1})$

Electronic configuration of $N^{\oplus}$

$(Z=7)\ (1s^2\ 2p_x^{\ 1} 2p_y^{\ 1}\ 2p_z^{\ 0})$

Electronic configuration of $O^{\oplus}$ (obtained after removal of one e^-) is exactly half-filled 2*p*-sub shell while this is not in the case of $N^{\oplus}$.

Since the removal of an electron from O gives a more stable arrangement than that of N; hence, IE_1 of O < IE_1 of N.

d. Similarly, IE_1 of *P* $(Z=15)\ (1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1)$ is greater than IE_1 of *S* $(Z=16)\ (1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1)$

e. Noble gases have the highest IE_1 in their respective period.

For example, IE_1 of Ne is higher than any other elements of the second period.

Similarly, IE_1 of Ar is higher than any other element of the third period. Because they have ns^2np^6 arrangement which is a stable electronic configuration hence the large amount of energy is required to remove an electron form such stable arrangement.

Note: The more stable the electronic configuration, the greater is the IE or $\Delta_i H^{\ominus}$.

1.13.3 VARIATION OF IE OR $\Delta_i H^{\ominus}$ IN THE PERIODIC TABLE

The IE_1 of the representative elements and noble gases given in Table 1.11 and IE_1 of elements having Z = 60 are plotted in Fig. 1.9.

Table 1.11 IE_1 of representative and noble gases (kJ mol^{-1})

1	→						18
	IE_1 increases along the period						
H 1312	2	13	14	15	16	17	He 2372
Li 520	Be 899	B 801	C 1086	N 1402	O 1314	F 1681	Ne 2080
Na 496	Mg 738	Al 577	Si 786	P 1011	S 999	Cl 1255	Ar 1520
K 419	Ca 590	Ga 579	Ge 760	As 946	Se 941	For 1142	Kr 1350
Rb 403	Sr 549	In 558	Sn 708	Sb 884	Te 869	I 1009	Xe 1170
Cs 374	Ba 502	Tl 589	Pb 715	Bi 703	Po 813	At 917	Rn 1037

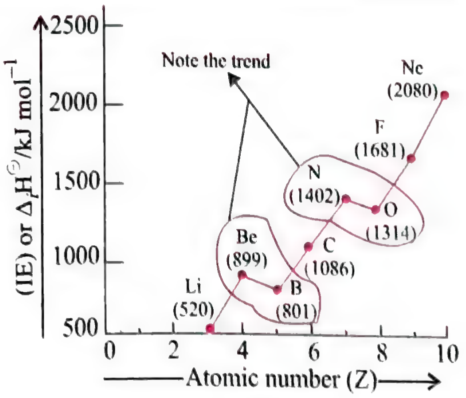
IE_1 decreases down in group ↓

[Note the trend in the elements circled]

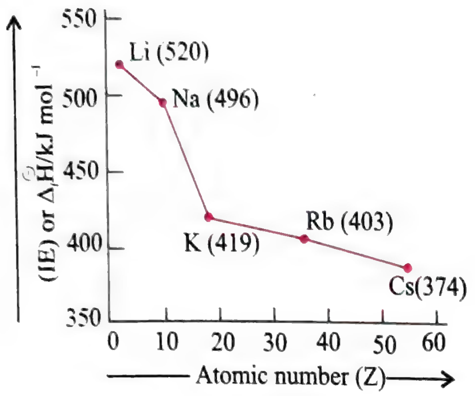
IE of an element mostly depends upon its electronic configuration and thus shown periodicity in the graph. There is a maxima at the noble gases which have closed electron shells and very stable electronic configuration. On the other hand, minima occurs at the alkali metals. Thus, alkali metals have the lowest IE_1 and hence have high activity.

On the contrary, noble gases with stable configuration (ns^2np^6) have highest IE_1 and hence are chemically inert.

Note: Cs have the lowest IE_1 and is the most electropositive elements.



(a)



(b)

Fig. 1.9 (a) First ionization enthalpies $\Delta_iH^{\ominus}$ of the second period as a function of atomic number (Z). (b) First ionisation enthalpies $\Delta_iH^{\ominus}$ of alkali metals as a function of atomic number (Z).

1.13.4 Variation of IE Across the Periods and Down the Group

1. IE_1 generally decreases down the group (↓).
2. IE_1 generally increases across the period (→). with exception as marked in Table 1.11 and Figs. 1.9, i.e. from Be to B, Mg to Al, N to O and P to S.

   The observed trends are explained on the basis of three factors:

   a. The attraction of electrons to the nucleus, i.e. on the basis of Z_{eff}.

   b. The repulsion of electrons from each other.

   c. Atomic radii (IE and atomic radii are closely related properties).

Explanation: Along the period (→), the nuclear charge (Z) increases and atomic radii decrease although shell remains the same. Due to these opposing factors, the outermost electrons are more strongly held by the nucleus, so more energy is required to remove the electrons. Hence IE_1 increases along the period (→).

However, some exceptions are observed in this general trend. These are due to: .

1. Extra stability of the half-filled and full-filled electronic configuration.
2. Types of electrons to be removed. Considering the IE_1 of the 2nd period elements:

   a. **Li to Be:** From Li to Be, IE_1 increases due to increase in nuclear charge and smaller atomic radii of Be than that of Li.

   b. **Be to B (exceptional case):** Although from Be to B nuclear charge increases, yet the IE_1 of Be > B (explained in section 1.12.1 (3)).

   c. **B to C and to N:** From B to C and to N, IE_1 increases due to the increasing nuclear charge and decreasing atomic radius.

   d. **N to O (exceptional case):** IE_1 of N should be less than IE_1 of oxygen, but the observed trend is IE_1 of N > IE_1 of O, as explained in Section 1.13.2 (5) (c) (i and ii).

   e. **O to F and to Ne:** IE_1 increases from O to F and to Ne, because of the increasing nuclear charge. Ne has the highest IE_1 in the 2nd period due to the stable noble gas configuration (ns^2, np^6).

   Similar trends in the IE_1 of the 3rd period have been observed.

1.13.5 Variations of IE Down the Group (↓)

IE_1 decreases down the group (↓) (see Table 1.11).

Explanation:

1. **Increase of atomic size:** Down the group (↓), the atomic size increases gradually due to the addition of new shell at each succeeding element. So, distance of the valence electrons from the nucleus increases. Consequently, the force of attraction between nucleus and outermost electron decreases and hence IE should decrease.
2. **Increase of screening effect:** The number of inner electrons increases with the addition of new shells thereby the screening effect increases. Thus, the force of attraction between the nucleus and the outermost electron further decreases and hence *IE should decrease*.
3. **Increase of nuclear charge (Z):** Z increases with the increase in atomic number, which results in the increase of force of attraction between the nucleus and the outermost electron and accordingly *IE should increase*.

The combined effect of the increase in the atomic size and the shielding effect compensate the effect of the increased nuclear charge. Consequently, the outermost electrons are held weakly by the nucleus and hence IE decreases down the group (↓).

Ion	$Cu^{\oplus}$	$Na^{\oplus}$
Size	0.96 Å	0.95 Å
Compound	CuCl	NaCl
Melting point	442°C	800°C

1.13.6 Importance of Ionisation Potential

A number of conclusions can be drawn from the concept of ionisation potential.

1. The elements having low values of ionisation potential readily lose their valency electrons and act as electropositive elements. These elements form cations and ionic compounds.
2. The elements having low values of ionisation potential act as strong reducing agents.
3. Stability of the various oxidation states of an element can be predicted. When the difference in ionisation potential ($\Delta_i H^{\oplus}$) of two successive states is aproximately 10 to 15 eV atom^{-1} (or 965–1450 kJ mol^{-1}) or less, the lower oxidation state is not stable one. For example, in case of Al, $\Delta_i H_1^{\ominus} = 6.0$, $\Delta_i H_2^{\ominus} = 18.8$, $\Delta_i H_3^{\ominus} = 28.4$ and $\Delta_i H_4^{\ominus} = 120$ eV atom^{-1} are the values of successive ionisation potential. Al^{4+} state is not possible because the $\Delta_i H_4^{\ominus}$ is very high.

   Differences in successive ionisation enthalpies are:

   $(\Delta_i H_2^{\ominus} - \Delta_i H_1^{\ominus}) = (18.8 - 6.0) = 12.8$ eV atom^{-1}

   $(\Delta_i H_3^{\ominus} - \Delta_i H_2^{\ominus}) = (28.4 - 18.8) = 96$ eV atom^{-1}

   $(\Delta_i H_4^{\ominus} - \Delta_i H_3^{\ominus}) = (120.0 - 28.4) = 91.6$ eV atom^{-1}

   Since the difference in the successive ionization enthalpies between $(\Delta_i H_2^{\ominus} - \Delta_i H_1^{\ominus})$ and $(\Delta_i H_3^{\ominus} - \Delta_i H_2^{\ominus})$ is less than 10–15 eV atom^{-1} and that of $(\Delta_i H_4^{\ominus} - \Delta_i H_3^{\ominus})$ is much more than 15 eV atom^{-1}. So, Al^{3+} is stable while $Al^{\oplus}$ and Al^{2+} are unstable.
4. When the difference in ionisation potential ($\Delta_i H^{\ominus}$) is about 16 eV atom^{-1} or more, the lower oxidation sate is stable one.

   For example, in the case of sodium (Na, Z = 11), $\Delta_i H_1^{\ominus} = 5.1$ and $\Delta_i H_2^{\ominus} = 47.3$ eV atom^{-1} are the successive IP, hence $Na^{\oplus}$ is a stable state and formation of Na^{2+} is not easy because high energy is required.
5. The elements with low values of IP are basic in character.

ILLUSTRATION 1.25

The first ionisation enthalpy ($\Delta_i H^{\ominus}$) values of the third period elements, Na, Mg and Si are respectively 496, 737 and 786 kJ mol^{-1}. Predict whether the first $\Delta_i H^{\ominus}$ value for Al will be more close to 575 or 760 kJ mol^{-1}? Justify your answer.

Sol. It will be more close to 575 kJ mol^{-1}. The value for Al should be lower than that of Mg because of the effective shielding of 3*p* electrons from the nucleus by 3*s*-electrons.

ILLUSTRATION 1.26

Calculate the energy required to convert all atoms of Mg to Mg^{2+} ions present in 48 mg of Mg vapours. IE_1 and IE_2 of Mg are 740 and 1450 kJ mol^{-1} respectively.

Sol. $Mg_{(g)} \rightarrow Mg^{\oplus}_{(g)} + e^-$; $IE_1 = 740$ kJ mol^{-1}

$Mg^{\oplus}_{(g)} \rightarrow Mg^{2+}_{(g)} + e^-$; $IE_2 = 1450$ kJ mol^{-1}

∴ Total energy required to convert 1 mol of of $Mg_{(g)}$ into $Mg^{2+}_{(g)}$ ion $= IE_1 + IE_2$

$= (740 + 1450)$ kJ mol^{-1}

$= 2190$ kJ mol^{-1}

$$48 \text{ mg of Mg} = \frac{48 \times 10^{-3}}{24} \text{ mol}$$

$$= 2 \times 10^{-3} \text{ mol}$$

∴ Energy required to ionise 2×10^{-3} mol of $Mg_{(g)}$

$$= 2190 \times 2 \times 10^{-3}$$

$$= 4.380 \text{ kJ}$$

ILLUSTRATION 1.27

The first (IE_1) and second (IE_2) ionisation energies (k J mol^{-1}) of a new elements designated by roman numerals are shown below:

	IE_1	IE_2
I	2370	5250
II	520	7300
III	900	1800
IV	1700	3400

Which of the above elements is likely to be:

a. A reactive metal

b. A reactive non-metal

c. A noble gas

d. A metal that forms a stable binary halide of the formula AX_2 (X = the halogen).

Sol.

a. Most reactive metal will be an alkali metal of the 1st group with its $IE_2 > IE_1$. Thus, the most reactive metal is II.

b. Most reactive non-metal will be a halogen of the 17th group. Its IE_1 will be quite high. Thus, most reactive non-metal is IV.

c. A noble gas will have very high IE_1. Thus, I is a noble gas.

d. A metal that forms a stable binary halide will be an alkaline earth metal of the 2nd group. Its IE_2 will not be much higher than IE_1. Thus, III is such a metal that forms a stable binary halide of formula AX_2.

ILLUSTRATION 1.28

The electronic configuration for some neutral atoms are given below.

A: $1s^2\ 2s^2$ B: $1s^2\ 2s^2 2p^3$

C: $1s^2\ 2s^2 2p^4$ D: $1s^2\ 2s^2\ 2p^6\ 3s^1$

In which of this electronic configuration would you expect to have highest (a) IE_1 and (b) IE_2.

Sol.

a. B: Because of exactly half-filled 2*p* subshell its IE_1 will be more than A and C.

b. D: Because after the removal of one electron, D will acquire a configuration of a noble gas and thus its IE_2 will be the highest.

ILLUSTRATION 1.29

The ionisation potential of hydrogen is 13.60 eV. Calculate the energy required to produce one mole of $H^{\oplus}$ ion (1 eV = 96.3 kJ mol^{-1}).

Sol. The ionisation potential may be represented as

$$H_{(g)} + 13.60\text{ eV} \rightarrow H^{\oplus}_{(g)} + e^-$$

We know 1 eV = 96.3 kJ mol^{-1}

$$13.60\text{ eV} = 96.3 \times 13.60 = 1309.68\text{ kJ}$$

Thus, energy per mol = 1309.68 kJ

ILLUSTRATION 1.30

Which of the following electronic configurations has the lowest value of ionisation energy? Explain.

a. $1s^2\,2s^22p^6$ **b.** $1s^2\,2s^22p^5$ **c.** $1s^2\,2s^22p^6\,3s^1$

Sol. The electronic configuration $1s^2, 2s^2\,2p^6, 3s^1$ has the lowest value of ionisation energy because the outermost electron $3s^1$ is far away from the nucleus. As a result atomic radius is the largest of the three and force of attraction between the nucleus and the outermost electron is less. Therefore, electron can be easily removed and has the lowest value of IE.

ILLUSTRATION 1.31

For each of the following pairs which has greater IE and why?

a. Li, $Li^{\oplus}$ **b.** K, Br **c.** Br, I **d.** $Na^{\oplus}$, Ne

Sol.

a. $Li^{\oplus}$. Because the size of $Li^{\oplus}$ is smaller and Z_{eff} is greater than the corresponding values of Li.

b. Br. Because Br has seven electrons in the outermost shell and has tendency to gain an electron rather than losing it. Moreover, the smaller size and high nuclear charge favour high IE for Br.

c. Br. It is due to the smaller atomic radius of Br than that of I.

d. $Na^{\oplus}$. As it has small atomic radius and high value of Z_{eff} than Ne.

ILLUSTRATION 1.32

Calculate the percentage of $Mg^{\oplus}_{(g)}$ and $Mg^{2+}_{(g)}$ if 2.4 g of Mg absorbs 120 kJ of energy. The IE_1 and IE_2 of $Mg_{(g)}$ are 740 and 1450 kJ mol^{-1}.

Sol. Moles of Mg $= \dfrac{2.4}{24} = 0.1$

Energy required in the conversion of 0.1 mol of $Mg_{(g)}$ to $Mg^{\oplus}_{(g)}$.

$$= 740 \times 0.1 = 74\text{ kJ}$$

Energy left unused = 120 – 74 = 46 kJ

So, 46 kJ of energy will be used to ionise $Mg^{\oplus}_{(g)}$ to $Mg^{2+}_{(g)}$

∴ Number of moles of $Mg^{\oplus}_{(g)}$ converted into

$$Mg^{2+}_{(g)} = \frac{46}{1450} = 0.03$$

Number of moles of $Mg^{\oplus}_{(g)}$ left = 0.1 – 0.03 = 0.07

$$\therefore \%\text{ of } Mg^{\oplus}_{(g)} = \frac{0.07}{0.1} \times 100 = 70\%$$

and % of $Mg^{2+}_{(g)}$ = 100 – 70 = 30%

ILLUSTRATION 1.33

The electronic configuration for the following atoms are given below:

a. $1s^2\,2s^22p^5$ b. $1s^2\,2s^2\,2p^4$ c. $1s^2\,2s^22p^6\,3s^2$

d. $1s^2\,2s^22p^6$ e. $1s^2\,2s^22p^6\,3s^1$

i. From the above configuration, arrange them in decreasing IE.

ii. Which of the electronic configuration given above will have the lowest IE?

iii. Which of the electronic configuration given above will be for noble gases?

Sol.

i. Arrange the electronic configuration of all the atoms in decreasing order of atomic number, in such a manner that atoms containing the same outer energy shell are grouped together, e.g.

$\underset{(c)}{1s^2\,2s^22p^63s^2(Z=12)} > \underset{(e)}{1s^2\,2s^22p^6\,3s^1(Z=11)}$... M-shell

$> \underset{(d)}{1s^2\,2s^22p^6(Z=10)} > \underset{(a)}{1s^2\,2s^22p^5(Z=9)} > \underset{(b)}{1s^2\,2s^22p^4(Z=8)}$ ...L shell

ii. Since the M-shell is far away from the nucleus than L-shell, so lesser amount of energy is required to remove an electron from M-shell than from L-shell.

Thus, the IE of atoms (c) and (e) should be lower than that of atoms (a), (b) and (d).

Moreover, in case of atom (c) the electron is to be removed from the more stable completely filled 3s-orbitals, whereas in case of atom (e) is not so.

Therefore, the IE of atom (c) should be higher than that of atom (e) [i.e. (c) > (e)].

The nuclear charge on atoms (d), (a) and (b) is +10, +9 and +8 respectively. Since the IE increases with the increase in nuclear charge so the decreasing order of IEs are:

(d) > (a) > (b)

Therefore, decreasing order of IEs of all the atoms is

(d) > (a) > (b) > (c) > (e)

From the above discussion it is clear that atom (e) has the lowest IE.

iii. The electronic configuration of atom (d) represents the noble gas $1s^2\,2s^22p^6$ since the configuration of noble gases is ns^2np^6.

ILLUSTRATION 1.34

The IE_1 and IE_2 (kJ mol^{-1}) of three elements A, B and C are given below:

	A	B	C
IE_1	400	550	1150
IE_2	2650	1070	2090

Identify the elements which represent (a) an alkali metal, (b) an alkaline earth metal or (c) non-metal.

Sol. **(a) (A)**

Since IE_2 of element (A) is very high as compared to IE_1, therefore it is an *alkali metal*.

(b) (B)

Since IE_1 of element (B) is higher than that of element (A) and lower than that of element (C), therefore it is an alkaline earth metal.

(c) (C)

Since IE_1 of element (C) is the highest of the two elements A and B, therefore it is a *non-metal*.

ILLUSTRATION 1.35

The sum of IE_1 and IE_2 and those of IE_3 and IE_4 in (kJ mol^{-1}) of Ni and Pt are:

	$(IE_1 + IE_2)$	$(IE_3 + IE_4)$	Total
Ni	2.5×10^3	8.8×10^3	11.3×10^3
Pt	2.7×10^3	6.7×10^3	9.4×10^3

a. What is the most common oxidation state (O.S.) of Ni and Pt.

b. Name the metal (Ni or Pt) which can more easily form compounds in its +4 O.S.

Sol. Thermodynamic stability of the transition elements and their compounds can be evaluated in terms of magnitude of IE's of metals. The smaller the IE of the metal, the stable is its compound.

a. Ni = +2 and Pt = +4.

Since $(IE_1 + IE_2)$ (2.5×10^3) of Ni is less than $(IE_1 + IE_2)$ of Pt, so, the most common oxidation states of Ni = +2. Similarly $(IE_3 + IE_4)$ of Pt is less than $(IE_3 + IE_4)$ of Ni, so, the most common oxidation state of Pt = +4.

b. Pt forms more stable complexes in +4 state due to its higher stability than +2 state.

ILLUSTRATION 1.36

The IE_1 of C atom is greater than that of boron (B) atom, whereas the reverse is true for IE_2. Explain?

Sol. The electronic configuration of C and B are as follows.

C: $1s^2\, 2s^2\, 2p^1_x 2p^1_y$

B: $1s^2\, 2s^2\, 2p^1_x$

Due to the higher nuclear charge (Z) in C, the force of attraction towards valency electrons is more in C atom and hence IE_1 of C > IE_1 of B.

After loss of one electron, the configuration of $C^{\oplus}$ and $B^{\oplus}$ is as follows:

$$C^{\oplus}: 1s^2\, 2s^2\, 2p^1_x \xrightarrow{\text{Easy}} C^{2+} + e$$

$$B^{\oplus}: \underset{\text{(Stable)}}{1s^2\, 2s^2} \xrightarrow{\text{Difficult}} B^{2+} + e$$

The $B^{\oplus}$ configuration is stable hence the removal of the 2nd electron is difficult in comparison to $C^{\oplus}$. Hence, IE_2 of B > IE_2 of C.

Note: The pairs in which IE_1 of first atom is greater than second atom whereas reverse order is true for IE_2.

(a) C > B (b) P > S (c) Be > B (d) Mg > Na

ILLUSTRATION 1.37

The second IE for alkali metals shows a jump while the third IE for alkaline metals shows a jump. Explain.

Sol. The alkali metals have ns^1 configuration while alkaline earth metals have ns^2 configuration.

So after IE_1, the alkali metals attain the inert gas configuration while the alkaline earth metals attain it after IE_2. Now the removal of electron from a noble gas configuration requires high IE_1 so there is a jump in the IE_2 for alkali and IE_3 for alkaline earth metals.

1.14 ELECTRON GAIN ENTHALPY ($\Delta_{eg}H^{\ominus}$) AND ELECTRON AFFINITY (EA)

When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying the process is defined as the **electron gain enthalpy** ($\Delta_{eg}H^{\ominus}$). Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion as represented by Eq. (1.1).

$$X_{(g)} + e \longrightarrow X^{\ominus}_{(g)} \qquad \text{...(1.1)}$$

Depending on the element, the process of adding an electron to the atom can be either endothermic or exothermic. For many elements energy is released when an electron is added to the atom and electron gain enthalpy is negative . For example, the halogens (group 17) have very high negative electron gain enthalpies because they can attain stable noble gas electronic configurations by picking up an electron.

On the other hand, noble gases have large positive electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration.

The electron gain enthalpies have large negative values towards the upper right of the periodic table preceding the noble gases.

1.14.1 Difference Between Electron Gain Enthalpy ($\Delta_{eg}H^{\ominus}$) and Electron Affinity

In many books, the negative of the enthalpy changed for the process depicted in Eq. (1.1) is defined as the electron affinity (EA) of the atom under consideration. If energy is released when an electron is added to an atom, the electron affinity is taken as positive, contrary to thermodynamic convention. If energy has to be supplied to add an electron to an atom, then the electron affinity of the atom is assigned a negative sign. However, *electron affinity is defined at absolute zero* and therefore at any other temperature heat capacities of the reactants and products have to be taken into account in $\Delta_{eg}H^{\ominus} = -EA - \frac{5}{2}RT$.

1.14.2 Successive Electron Gain Enthalpies

After the addition of one electron the atom becomes negatively charged and the second electron is to be added to a negatively charged ion. But the addition of the second electron is opposed by the electrostatic repulsion and hence the energy is required for the addition of second electron.

Thus, the second electron gains enthlpy of an element is positive. For example, when an electron is added to oxygen atom to form $O^{\ominus}$ ion, energy is released. But when another electron is added to $O^{\ominus}$ ion to form O^{2-} ion, energy is required or absorbed to overcome the strong electrostatic repulsion between the negatively charged $O^{\ominus}$ ion and the incoming electron being added. Thus,

(First electron gain enthalpy) ($\Delta_{eg}H_1^{\ominus}$):

$O_{(g)} + e^- \longrightarrow O^{\ominus}_{(g)}$, $\Delta_{eg}H_1^{\ominus} = -140\ \text{kJ mol}^{-1}$

(Exothermic process)

(Second electron gain enthalpy) ($\Delta_{eg}H_2^{\ominus}$):

$O^{\ominus}_{(g)} + e^- \longrightarrow O^{2-}_{(g)}$, $\Delta_{eg}H_2^{\ominus} = +780\ \text{kJ mol}^{-1}$

(Endothermic process)

Likewise $\Delta_{eg}H_2^{\ominus}$ of S is also positive.

For example,

$S_{(g)} + e^- \longrightarrow S^{\ominus}_{(g)}$, $\Delta_{eg}H_1^{\ominus} = -200\ \text{kJ mol}^{-1}$

(Exothermic process)

$S^{\ominus}_{(g)} + e^- \longrightarrow S^{2-}_{(g)}$, $\Delta_{eg}H_2^{\ominus} = +600\ \text{kJ mol}^{-1}$

(Endothermic process)

1.14.3 Units of $\Delta_{eg}H^{\ominus}$/EA

Like IE, $\Delta_{eg}H^{\ominus}$ or EA is measured either in eV atom^{-1} or kJ mol^{-1}.

1.14.4 Variations of $\Delta_{eg}H^{\ominus}$ in the Periodic Table

1. a. Generally, $\Delta_{eg}H_1^{\ominus}$ decreases (less negative) down the group (↓).
   b. Generally, $\Delta_{eg}H_1^{\ominus}$ increases (more negative) along the period (→).
   But from Table 1.12, it is evident that $\Delta_{eg}H^{\ominus}$ does not show perfectly regular trend along the period (→) and down the group (↓) because of a number of exceptions.
2. **Variation of $\Delta_{eg}H^{\ominus}$ along the period (→):**
   Generally, $\Delta_{eg}H^{\ominus}$ increases (more –ve) along the period (→).
   Explanation: The Z_{eff} increases and atomic sizes decrease along the period (→) and consequently it will be easier to add an electron to a smaller atom since the added electron on an average would be closer to the positively charged nucleus. Hence, $\Delta_{eg}H^{\ominus}$, in general, increases (more and more –ve) along the period (→).
3. **Variation of $\Delta_{eg}H^{\ominus}$ down the group (↓):**
   Generally, $\Delta_{eg}H^{\ominus}$ decreases (less negative) down the group (↓).
   Explanation: Both the atomic size and Z_{eff} increase down the group (↓). But the effect of atomic size is much more predominating than Z_{eff}. Thus, with increases in atomic size, the attraction between the nucleus and incoming electron decreases and hence the $\Delta_{eg}H^{\ominus}$ decreases (becomes less negative).

1.14.5 Factors on which $\Delta_{eg}H^{\ominus}$ Depends

It depends on the following factors.

1. **Size of atom:** In general, the $\Delta_{eg}H^{\ominus}$ value decreases (less negative) with increasing atomic radius or size of an atom.

$$\Delta_{eg}H^{\ominus} \text{ or EA} \propto \frac{1}{\text{Atomic radius}}$$

Explanation: The larger the size of an atom, the larger is the distance between the nucleus and the last shell which receives the incoming electron. As a result, force of attraction between the nucleus and the incoming electron decreases and hence $\Delta_{eg}H^{\ominus}$ decreases (less negative value, i.e. energy released is lesser) (see Table 1.12).

Table 1.12 $\Delta_{eg}H^{\ominus}$ of some elements in kJ mol^{-1}

Pe-riod	Group →						Note the trend	
↓	1	2	13	14	15	16	17	18
1	H –73							He (+48)
2	Li –60	Be (~0)	B –23	C –122	N +20.1	O –141	F –328	Ne (+116)
3	Na –53	Mg (~0)	Al –44	Si –119	P –74	S –200	Cl –349	Ar (+96)
4	K –49	Ca (~0)	Ga –36	Ge –116	As –77	Se –195	Br –324.5	Kr (+96)
5	Rb –47	Sr (~0)	In –34	Sn –120	Sb –101	Te –190	I –295	Xe (+77)
6	Cs –46	Ba (~0)	Tl –30	Pb –101	Bi –110	Po –174	At –270	Rn (+68)

2. **Effective nuclear charge (Z_{eff}):** The higher the Z_{eff}, the greater is the tendency of the atom to attract the incoming electron towards itself and hence the higher the amount of energy is released (i.e. $\Delta_{eg}H^{\ominus}$ becomes more –ve).
3. **Electronic configuration:** Elements with half-filled or full-filled orbitals are more stable. As a result, energy is required to add an incoming electron, since they do not accept the incoming electron so easily.
   Hence, $\Delta_{eg}H^{\ominus}$ have high positive value. The effect of this factor on the magnitude of $\Delta_{eg}H^{\ominus}$ of an element can be understood by the following examples:
   a. **$\Delta_{eg}H^{\ominus}$ values of the 2nd groups:** *ns*-orbital of the valence shell of the atoms of the 2nd group is completely filled and the addition of an extra electron to this *ns*-orbital is not possible. Consequently, the elements of the 2nd group have practically zero $\Delta_{eg}H^{\ominus}$.
   b. **$\Delta_{eg}H^{\ominus}$ values of N and P:** The valence shell of N and P are:
   $N = 2s^2\,2p^3$; $P = 3s^2\,3p^3$
   2*p*- and 3*p*-orbitals in N and P respectively are half-filled, and hence are extraordinary stable. Thus, the addition of an extra electron to these orbitals is not

possible. Consequently, N and P have law $\Delta_{eg}H^{\ominus}$ values (N = + 20.1 and P = –74 kJ mol^{-1}).

c. **$\Delta_{eg}H^{\ominus}$ of halogens:** The valence shell configuration of halogens ($ns^2\ np^5$) requires one electron to stabilise its configuration by attaining stable noble gas configuration ($ns^2\ np^6$).

Thus, halogens have a strong tendency to accept one electron. Consequently, they have very high negative values of $\Delta_{eg}H^{\ominus}$.

However, from Cl to I, $\Delta_{eg}H^{\ominus}$ decreases, i.e. becomes less and less negative due to the corresponding increase in the size of the atoms. In Cl, the incoming electron is added in 3*p*-subshell, in Br it adds in 4*p*-subshell while in I it adds to the 5*p*-subshell.

As the distance between the nucleus and the sub-shell increases, the attraction between the incoming electron and nucleus decreases, hence $\Delta_{eg}H^{\ominus}$ decreases (i.e. less negative) along the period (→) from Cl to Br to I.

Exception (I): Generally, $\Delta_{eg}H^{\ominus}$ decreases (i.e. becomes less and less –ve) down the group (↓). So, the decreasing order of $\Delta_{eg}H^{\ominus}$ should be F > Cl > Br > I.

But the *actual order* observed is as follows

	Cl	>	F	>	Br	>	I
EN:	–349		–333		–325		–295

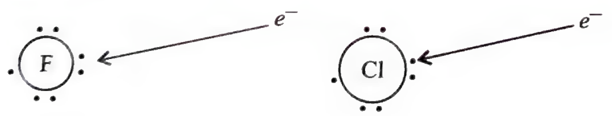
Note: $\Delta_{eg}H^{\ominus}$ of F is lower (i.e., less negative) than that of Cl.

It is due to the very small size of F atom. There is strong electron–electron repulsion in the relatively small 2*p* orbitals of F and thus, the incoming electron does not experience much attraction. Hence, the incoming electron is not added easily as it is added in large 3*p*-orbitals of Cl.

Consequently, the $\Delta_{eg}H^{\ominus}$ of F is less negative than that of Cl.

Note: Among halogens, Cl has the highest (most –ve) $\Delta_{eg}H^{\ominus}$.

Alternatively:



Due to the very small size of F atom, the incoming electron experiences a strong repulsion between the seven non-bonding electrons on the F atom and incoming electron. So, the incoming electron is added with difficulty. However, due to the large size of Cl atom the incoming electron experiences very less repulsion between the seven non-bonding electrons and incoming electron. Consequently, the $\Delta_{eg}H^{\ominus}$ of F is less negative than that of Cl.

Exception (II): Similarly, $\Delta_{eg}H^{\ominus}$ of some of the elements of the 2nd period have less (–ve) value than the corresponding elements of the 3rd period. For example,

$\Delta_{eg}H^{\ominus}$ of some elements are as follows: (see Table 1.12)

$$\begin{pmatrix} B < Al, \\ -23 < -44 \end{pmatrix}\begin{pmatrix} N < P, \\ +20 < -74 \end{pmatrix}\begin{pmatrix} O < S, \\ -141 < -200 \end{pmatrix}$$

and $\begin{pmatrix} F < Cl \\ -322 < -349 \end{pmatrix}$ in kJ mol^{-1}

The same explanation as given in exception (I).

1.14.6 $\Delta_{eg}H^{\ominus}$ of Noble Gases

Inert gases have completely filled subshells ($ns^2\ np^6$), therefore the incoming electron has to enter the next higher principle quantum level leading to a very unstable electronic configuration. As a result, energy is required to add an additional electron. That is why $\Delta_{eg}H^{\ominus}$ of noble gases have large positive values.

Down the group (↓), the size of the atom increases and hence $\Delta_{eg}H^{\ominus}$ have lower positive values.

$\Delta_{eg}H^{\ominus}$ of Ar (+ 96) is lower than that of Ne (+ 116).

However, $\Delta_{eg}H^{\ominus}$ of He is the lowest (+ 48) of all the inert gases. This unexpected behaviour is due to its smallest size so it has much higher tendency to accept an incoming electron than any other inert gases.

1.14.7 Importance of Electron Gain Enthalpy

Certain properties of the elements are predicted on the basis of values of electron gain enthalpy.

1. The elements having high (–ve) values of electron gain enthalpy are capable of accepting electron easily. They form anions and electrovalent compounds. These elements are electronegative in nature.
2. The elements having high (–ve) values of electron gain enthalpy act as strong oxidising agents, for example, F, Cl, Br, O, S etc.

On the basis of the general trend of ionisation potential and electron gain enthalpy, the following properties can be predicted:

a. Metallic nature decreases in a period while non-metallic nature increases. Metallic nature increases in a group while non-metallic nature decreases. The arrow (↓) represents a group and (→) represents a period.

Metallic (electropositive): → Decreases; ↓ Increases

Non-metallic (electronegative): → Increases; ↓ Decreases

b. Reducing nature decreases in a period while oxidising nature increases. The reducing nature increases in a group while oxidising nature decreases.

Reducing nature: → Decreases; ↓ Increases

Oxidising nature: → Increases; ↓ Decreases

c. Stability of the metal increases while the activity of the metal decreases in a period and in a group stability decreases while the activity increases.

Stability of the metal

Stability of the metal $\longrightarrow$ Increases; Decreases $\downarrow$

Activity of the metal

Activity of the metal $\longrightarrow$ Decreases; Increases $\downarrow$

This trend is observed especially in 1, 2 and 13 group elements.

d. The basic nature of the oxides decreases in a period while acidic nature increases. In a group, basic nature increases while acidic nature decreases.

Basic nature of oxides

Basic nature of oxides $\longrightarrow$ Decreases; Increases $\downarrow$

Acidic nature of oxides

Acidic nature of oxides $\longrightarrow$ Increases; Decreases $\downarrow$

ILLUSTRATION 1.38

Which of the following will have the most negative electron gain enthalpy and which the least negative?
P, S, Cl, F. Explain your answer.

Sol. Electron gain enthalpy generally becomes more negative across a period as we move from the left to the right. Within a group, electron gain enthalpy becomes less negative down a group. However, adding an electron to the 2*p*-orbital leads to the greater repulsion than adding an electron to the larger 3*p*-orbital. Hence, the element with the most negative electron gain enthalpy is chlorine; and the one with the least negative electron gain enthalpy is phosphorus.

$Cl > F > S > P$

ILLUSTRATION 1.39

The amount of energy released when 10^{12} atoms of Cl vapours are converted to $Cl^{\ominus}$ ions, according to the equation:

$Cl_{(g)} + e^- \longrightarrow Cl^{\ominus}_{(g)}$ is -58×10^{-10} J atom^{-1}

Calculate the $\Delta_{eg}H^{\ominus}$ of Cl atom in kJ mol^{-1} and eV atom^{-1}.

Sol. The amount of energy released when 1 mol ($\approx 6.0 \times 10^{23}$ atoms) of Cl are converted to $Cl^{\ominus}$ ions according to the above equation is $\Delta_{eg}H^{\ominus}$ of Cl vapours.

$\therefore \Delta_{eg}H^{\ominus}$ of Cl vapours

$$= \frac{-58 \times 10^{-10}\,\text{J} \times 6 \times 10^{23}}{10^{12}}$$

$$= -348 \times 10\ \text{J mol}^{-1}$$

$$= -3.48\ \text{kJ mol}^{-1}$$

We know that

$1\ \text{eV atom}^{-1} = 96.49\ \text{kJ mol}^{-1}$

Therefore, $\Delta_{eg}H^{\ominus}$ of Cl vapours in eV is

$$\frac{-3.48}{96.49} = -0.036\ \text{eV atom}^{-1}$$

ILLUSTRATION 1.40

The electron gain enthalpy of chlorine is 3.7 eV. How much energy in kJ and kcal is released when 1 g of chlorine is converted completely to $Cl^{\ominus}$ ion in the gaseous state. (1 eV = 96.3 kJ mol^{-1})

Sol.

a. The electron gain enthalpy in kJ is represented as

$$Cl_{(g)} + e^- \longrightarrow Cl^{\ominus}_{(g)} + 3.7\ \text{eV}$$

Now, 1 eV atom^{-1} = 96.3 kJ mol^{-1}

$\therefore\ 3.7\ \text{eV} = 3.7\ \text{eV} \times 96.3\ \text{kJ mol}^{-1}$

Energy released when 35.5 g (1 mole) of chlorine is completely converted to $Cl^{\ominus}_{(g)}$ ion = 3.7×96.3 kJ

Energy released when 1 g of chlorine is completely converted to $Cl^{\ominus}_{(g)}$ ion $= \dfrac{3.7 \times 96.3}{35.5} = 10.04$ kJ

b. $\Delta_{eg}H^{\ominus}$ in kcal

(1 eV = 23.06 kcal mol^{-1})

$$\therefore\ \Delta_{eg}H^{\ominus} = \frac{3.7 \times 23.06}{35.5} = 2.4\ \text{kcal}$$

ILLUSTRATION 1.41

Write the electronic configuration of the element with atomic number of 9, 11, 21 and 36. Predict the following from these configurations:

a. Which of them has the lowest ionisation potential?
b. Which of them has the highest electron gain enthalpy?
c. Which of them are non-metals?
d. Which of them has zero electron gain enthalpy?

Sol. The electronic configuration of the given elements are

Atomic number

9 : $1s^2\,2s^2\,2p^5$

11 : $1s^2\,2s^2 2p^6\,3s^1$

21 : $1s^2\,2s^2 2p^6\,3s^2 3p^6\,4s^2\,3d^1$

36 : $1s^2\,2s^2 2p^6\,3s^2 3p^6\,4s^2 4d^{10} 4p^6$

a. The element with atomic number 11 has the lowest ionisation potential.

Reason: Because after losing the most loosely bound electron it acquires a stable configuration.

b. The element with atomic number 9 has the highest electron gain enthalpy.

Reason: Tendency to acquire stable configuration on receiving an electron.

c. The element with atomic numbers 9 and 36 are non-metals.

d. The elements with atomic number 36 has zero electron gain enthalpy.

ILLUSTRATION 1.42

Which of the following has the highest electron gain enthalpy. Give reasons.

a. $[Ne]3s^23p^3$ b. $[Ne]3s^23p^4$
c. $[Ne]3s^23p^5$ d. $[Ne]3s^23p^6$

Sol. Atomic number (Z) of (a), (b), (c) and (d) respectively are:

a. $Z = 10 + 5 = 15$. Element is P.
b. $Z = 10 + 6 = 16$. Element is S.
c. $Z = 10 + 7 = 17$. Element is Cl.
d. $Z = 10 + 8 = 18$. Element is Ar.

The element chlorine corresponding to electronic configuration (c) has the highest electronic affinity. Halogens have $ns^2\ np^5$ configurations due to which halogens show a strong tendency to accept an electron to acquire inert gas configuration ($ns^2\ np^6$). Therefore, (c) the highest (–ve) electron gain affinity value due to its very small size.

ILLUSTRATION 1.43

Arrange the elements with the following electronic configuration of valence electron in decreasing order of $\Delta_{eg}H^\ominus$.

a. $3s^23p^4$ b. $2s^22p^4$
c. $2s^22p^3$ d. $2s^22p^5$

Sol. c > b > a > d (N > O > S > F)

Elements (b), (c) and (d) are of the 2nd period namely O, N and F respectively, whereas element (a) is of the 3rd period and is S atom.

Out of F, O, N and S, only N has (+ve) $\Delta_{eg}H^\ominus$ because of its stable half-filled electronic configuration. F, O and S have (–ve) $\Delta_{eg}H^\ominus$. But F has the most –ve $\Delta_{eg}H^\ominus$, since it requires one electron to acquire the nearest inert gas configuration.

Out of O and S, O has the less – ve $\Delta_{eg}H^\ominus$ than S because of electron–electron repulsion present in its small and compact 2p-orbital.

Thus decreasing order of $\Delta_{eg}H^\ominus$ is

c > b > a > d (N > O > S > F)

ILLUSTRATION 1.44

Which one of the following pairs has higher $\Delta_{eg}H^\ominus$?

a. $S^\ominus$, O b. $N^\ominus$, P
c. S, $O^\ominus$ d. $O^\ominus$, $S^\ominus$

Sol.

a. $S^\ominus > O$

Due to repulsion between the electrons on $S^\ominus$ and the additional incoming electrons $\Delta_{eg}H^\ominus$ of $S^\ominus$ = + ve unlike that of O is –ve.

b. $N^\ominus > P$

Due to repulsion between the electrons on $N^\ominus$ and the addition incoming electron $\Delta_{eg}H^\ominus$ of $N^\ominus$ = + ve while that of P is – ve.

c. $O^\ominus > S$. (Same explanation as in (a) and (b).

d. $O^\ominus > S^\ominus$

Due to small size of O atom, repulsion between the electrons on $O^\ominus$ and the additional incoming electron is much more than in $S^\ominus$.

Hence, $\Delta_{eg}H^\ominus$ of $O^\ominus$ is more +ve than that of $S^\ominus$.

ILLUSTRATION 1.45

Give the decreasing order of $\Delta_{eg}H^\ominus$ of the following elements: B, C, N, O.

Sol. **N > B > C > O**

Explanation: N has +ve $\Delta_{eg}H^\ominus$ because of its stable half-filled electronic configuration. Whereas in case of B, C and O, since the size decreases along the period (→) i.e., from B to C and to O, thus $\Delta_{eg}H^\ominus$ becomes more and more –ve from B → C → O.

Thus, the overall decreasing order of $\Delta_{eg}H^\ominus$ is N > B > C > O.

ILLUSTRATION 1.46

How many Cl atoms can you ionise in the process $Cl \rightarrow Cl^\oplus + e^-$ by the energy liberated for the process $Cl + e^- \rightarrow Cl^\ominus$ for one Avogadro number of atoms. Given IP = 13.0 eV and EA = 3.60 eV.

Sol. Let n atoms be ionised.

$$6.02 \times 10^{23} \times EA = n \times IP$$

$$n = \frac{6.02 \times 10^{23} \times 3.60}{13} = 1.667 \times 10^{23} \text{ atoms}$$

1.15 ELECTRONEGATIVITY AND ELECTROPOSITIVITY

Electronegativity (EN) is defined as the tendency of an atom to attract shared pair of electrons towards itself in a covalently bonded molecules. It is represented as χ (pronounced as (chi) or EN.

It may be noted that both IE and $\Delta_{eg}H^\ominus$ relate to atoms in their gaseous isolated state, whereas EN is a property of an atom in the bonded state.

Unlike IE and $\Delta_{eg}H^\ominus$, it is not a measurable quantity. However, a number of numerical scales of EN of elements, e.g. Pauling scale, Mulliken–Jaffe scale, Allred–Rochow scale and Sanderson's have been developed. The most widely used is the Pauling scale. Linus Pauling, an American scientist in 1922 assigned arbitrarily a value of **4.0 to F (fluorine)**, which has the greatest ability to attract electrons.

The EN of any element is not constant. It varies depending on the element to which it is bound. Although it is not a measurable quantity, yet it provides a means of predicting the nature of force that holds a pair of atoms together.

Electropositivity (EP) is a measure of an element's ability to donate electrons, and therefore form positive ions; thus, it is opposed to electronegativity. Mainly, this is an attribute of metals, meaning that for the most part, the greater the metallic character of an element, the greater the electropositivity. Therefore, the alkali metals are most electropositive of all. This is because they have a single electron in their outer shell and as this is relatively far from the nucleus of the atom, it is easily lost; in other words, these metals have low ionisation energies.

While, electronegativity increases along periods in the periodic table, and decreases down groups, electropositivity decreases along periods (from the left to the right) and increases down the groups.

Electropositive shark repellent utilises electropositive metals as shark repellents, since they generate measurable voltages in a seawater electrolyte relative to a shark.

1.15.1 Variation of EN in the Periodic Table

1. EN generally increases along the period (→), i.e. from lithium (Li) to fluorine (F) in the periodic table.
2. EN generally decreases down the group (↓), i.e. from fluorine (F) to astatine (At) in the periodic table.

Note: F is the most EN element with a value of (4.0) (Pauling scale) and Cs is the least EN element.

There are some exceptions to this general rule:

a. Gallium and germanium have higher electronegativities than aluminium and silicon respectively because of the *d*-block contraction.

b. Elements of the fourth period immediately after the first row of the transition metals have unusually small atomic radii because the 3*d*-electrons are not effective at shielding the increased nuclear charge, and smaller atomic size correlates with higher electronegativity (see Allred–Rochow electronegativity.

c. The anomalously high electronegativity of lead, particularly when compared to thallium and bismuth, appears to be an artifact of data selection /(and data availability)—methods of calculation other than the Pauling method show the normal periodic trends for these elements.

1.15.2 Group Electronegativity

In organic chemistry, electronegativity is associated more with different functional groups than with individual atoms. The terms **group electronegativity** and **substituent electronegativity** are used synonymously. However, it is common to distinguish between the inductive effect and the resonance effect, which might be described as σ- and π-electronegativities respectively. There are a number of linear free-energy relationships which have been used to quantify these effects, of which the Hammett equation is the best known. Kabachnik parameters are group electronegativities for use in organophosphorus chemistry.

1.15.3 Factors Affecting the Magnitude of Electronegativity

1. **Atomic radius:** As two atomic radius of the element increases the EN value decreases.

$$\text{EN} \propto \frac{1}{\text{Atomic radius}}$$

Explanation: Atomic radii tend to decrease along the period (→) and increases down the group (↓). The attraction between the outer (or valence) electrons and the nucleus increases as the atomic radius decreases in a period. Therefore, EN also increases. Likewise, EN values decrease with the increase in atomic radii down a group. This trend is similar to that of IE.

2. **Effective nuclear charge (Z_{eff}):** The EN value increases as the Z_{eff} on the atomic nucleus increases.

$$\therefore \quad \text{EN} \propto Z_{eff}$$

3. **Number of inner shells:** The atom with greater number of inner shells has less value of EN than the atom with smaller number of inner shells.

$$\therefore \quad \text{EN} \propto \frac{1}{\text{Number of inner shells}}$$

For example, EN values of halogens decrease from F(Z = 9) to At (Z = 85), since the number of inner shell increases in the same order. Decreasing order of EN of halogens is

$\therefore$ F (4.0) > Cl (3.0) > Br (2.8) > I (2.5) > At (2.2)

4. **Charge on the ion or oxidation state of the atom:** The EN increases as the oxidation state (OS), i.e. the number of positive charge of the atom increases. But the EN decreases as the negative charge of the atom increases.

$$\left(\begin{array}{l}\text{EN} \propto +\text{ve charge} \\ \text{and EN} \propto \dfrac{1}{-\text{ve charge}}\end{array}\right)$$

Explanation: A cation attracts the electron pair more rapidly towards itself than its parent atom. This is due to smaller size of the cation as compared to its parent atom (i.e. size of $M^{\oplus}$ < size of M). Thus a cation has higher EN than its parent atom. (EN of $M^{\oplus}$ > EN of M), e.g.

Decreasing order of EN = $M^{3+} > M^{2+} > M^{1+} > M...$

Order of size = $M > M^{+} > M^{2+} > M^{3+}$ for example, the decreasing order of EN of some atoms and their ions.

a. Fe^{3+} (1.96) > Fe^{2+} (1.83) > Fe(1.8)

b. Pb^{4+} (2.33) > Pb^{2+} (1.87) > Pb (1.80).

An anion has less tendency to attract the electron pair than its parent atom. This is due to larger size of the anion as compared to its parent atom (i.e. size of $X^{\oplus}$ > size X). Thus, an anion has less EN than its parent atom.

$\therefore$ Decreasing order of EN = $X > X^{\ominus} > X^{2-}$

Decreasing order of size = $X^{2-} > X^{\ominus} > X$

For example, $F^{\ominus}$ ion has less EN value (0.8) than F atom (4.0).

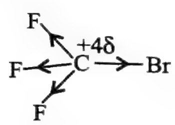
The chemical effects of this increase in electronegativity can be seen both in the structure of oxides and halides and in the acidity of oxides and oxoacids. Hence CrO_3 and Mn_2O_7 are acidic oxides with low melting points, while Cr_2O_3 is amphoteric and Mn_2O_3 is a completely basic oxide.

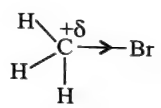
The effect can also be clearly seen in the dissociation constants of the oxoacids of chlorine. The effect is much larger than could be explained by the negative charge being shared among a larger number of oxygen atoms, which would lead to a difference in pK_a of $\log_{10}(1/4) = -0.6$ between hypochlorous acid and perchloric acid. As the oxidation state of the central chlorine atom increases, more electron density is drawn from the oxygen atoms on to the chlorine, reducing the partial negative charge on the oxygen atoms and increasing the acidity.

5. **Nature and number of atoms (i.e. substituent attached to the atom):** It is evident that EN of an atom is not the property of this atom in its isolated state but it depends on the number and nature of the atoms to which it is bonded. For this reason EN value of an atom is not constant.

   For example, EN of P atom in PCl_3 molecule is less than that in PF_5 molecule.

   Similarly, EN of C atom in CF_3Br is more than in CH_3Br, because C-atom in CF_3Br acquires greater positive charge than in CH_3Br.





6. **State of hybridisation:** The magnitude of EN increases as the *s*-character in the hybrid orbitals increases because *s*-electrons are comparatively near to the nucleus, and are more attracted or penetrated into the nucleus.

   For example, the EN values of C-atom in CH_4 (sp^3), ethene (sp^2) and ethyne or acetylene (sp) are shown below in increasing order,

a.	Hydrocarbon	CH_4	$CH_2=CH_2$	$HC\equiv CH$
b.	Hybridisation state	sp^3	sp^2	sp
c.	*s*-character	25%	33.33%	50%
d.	EN values of C	2.48	2.75	3.25

$\xrightarrow{\text{Increasing order of EN}}$

   It implies that CH_4 is unreactive, ethene is more reactive while ethyne is highly reactive.

   Moreover, the highest value of EN of C-atom in ethyne also accounts for its highly acidic hydrogen atom, i.e. acidic properties of ethyne.

7. **Ionisation energy (IE) and electron gain enthalpy ($\Delta_{eg}H^{\ominus}$):** Higher IE of an atom means that it is difficult to remove the most loosely bonded electron from the atom which also means that $\Delta_{eg}H^{\ominus}$ of that atom will also be greater.

   Thus, the atoms which have high positive values of IE and $\Delta_{eg}H^{\ominus}$ also have higher values of EN.

   For example, halogens (group 17) which have the highest IE and $\Delta_{eg}H^{\ominus}$ also have highest values of EN.

   Similarly, alkali metals (group 1) which have the lowest IE and $\Delta_{eg}H^{\ominus}$ have the lowest values of EN.

1.15.4 Applications of EN

The concept of EN is used to predict the metallic, non-metallic character of elements and polarity of bonds.

1.15.4.1 Metallic and Non-metallic Properties

1. Non-metallic elements have strong tendency to gain electrons.

   $\therefore$ EN $\propto$ Non-metallic properties of elements

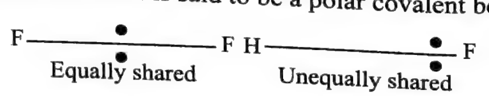
   $$\text{(OR) EN} \propto \frac{1}{\text{Metallic properties of elements}}$$

2. Thus, the increase in EN along the period (→) increases the non-metallic character (or decreases the metallic character) of elements.
3. Similarly, the decrease in EN down the group (↓) decreases the non-metallic character (or increases metallic character) of elements.

1.15.4.2 Polarity of Covalent Bond

In all homonuclear diatomic molecules such as hydrogen molecule (H_2), chlorine molecule (Cl_2), fluorine molecule (F_2), oxygen molecule (O_2), the electron pair or pairs is shared equally between the two atoms. This means that the shared electrons are equally attracted to both the nuclei and therefore spend equal amounts of time near each nucleus. As a result, the molecule is neutral non-polar.

In the heteronuclear diatomic molecule the bonding is different. Electronegative is defined as the tendency of an atom to attract electrons towards itself in a chemical bond. Thus, in heteronuclear diatomic molecule, both the atoms joined by the covalent bond possess different electronegativities. As a result, the atom having higher value of electronegativity attracts the shared electron pair much more strongly than the other atom. For example, in HF the electron pair is more attracted towards F as it is more electronegative than hydrogen. Due to this, the fluorine end of the molecule appears negative and the hydrogen end positive. Such molecules having two oppositely charged poles are called polar molecules and the bond is said to be a polar covalent bond.



A covalent bond, in which electrons are shared unequally and the bonded atoms acquired a partial positive and negative charge, is called a polar covalent bond or a covalent bond between two dissimilar atoms is a polar covalent bond. Two kinds of notation are used to indicate a polar covalent bond.

$\overset{\delta+}{H} - \overset{\delta-}{F}$ or $\overrightarrow{H - F}$

Polar covalent bonds may be thought of as being intermediate between the non-polar bond and the pure ionic bond.

1.15.4.3 Characteristics of Polar Bond

1. The polarity of the molecule is determined from their dipole moment (μ) values. Higher the difference in EN of two bonded atoms, the higher is the dipole moment (μ) of the molecule.
2. **Ionic character in a polar covalent bond:** The concept of EN is also used to know the nature of bond and to calculate the percentage of ionic character in a polar covalent bond. These trends are summarised below:

   (where χ_A and χ_B are the EN values of atoms A and B in AB molecule)

   a. When $\chi_A = \chi_B$, then A–B bond is non-polar covalent bond or simply covalent bond, eg. H_2, Cl_2 and N_2 moleules.

   b. Where $\chi_A > \chi_B$ i.e. $\chi_A - \chi_B$ is small, then A–B bond is polar covalent bond and is represented as $A^{\delta-}$–$B^{\delta+}$, since $\chi_A > \chi_B$.

   For example, both O–H covalent bonds in H_2O molecule are polar covalent ponds and are represented as $O^{\delta-}$–$H^{\delta+}$, Since $\chi_O > \chi_H$ and $\chi_O - \chi_H$ is small.

   c. When $\chi_A >> \chi_B$ i.e. $\chi_A - \chi_B$ is very large, A–B bond is an ionic or polar bond and is represented As $A^{\ominus}$–$B^{\oplus}$, since $\chi_A >> \chi_B$. For example, NaCl molecule is an ionic bond and is represented as $Na^{\oplus}Cl^{\ominus}$ (here Cl = A and Na is B).

1.15.4.4 Percentage of Ionic Character in Polar Covalent Bond

It two atoms A and B are linked by a polar covalent bond, the percentage of ionic character in this bond depends on the difference of EN values of A and B.

1. Greater the difference ($\chi_A - \chi_B$), greater is the percentage of ionic character in A–B bond.
2. When ($\chi_A - \chi_B$) = 1.7, the bond is 50% ionic and 50% covalent.
3. When ($\chi_A - \chi_B$) < 1.7, the ionic character in $A^{\delta-}$–$B^{\delta+}$ is less then 50% and that of covalent character is more than 50%. Thus $A^{\delta-}$–$B^{\delta+}$ is **predominantly covalent.**
4. When ($x_A - x_B$) > 1.7, the ionic character in $A^{\delta-}$–$B^{+\delta}$ is more than 50% and that of covalent character is less than 50%, hence $A^{\delta-}$–$B^{\delta+}$ bond is **predominantly ionic.**

   Ionic character and stability of bond decreases as difference in electronegativity decreases $\longrightarrow$

   SiH_4, NCl_3, PH_3 and AsH_3 are unstable. Their EN differences are given below:

   EN differences in $SiH_4 = (\chi_H - \chi_{Si} = 2.1 - 1.8 = 0.3)$

   EN differences in $NCl_3 = (\chi_N - \chi_{Cl} = 3.0 - 3.0 = 0.0)$

   EN differences in $PH_3 = (\chi_P - \chi_H = 2.1 - 2.1 = 0.0)$

   EN differences in $AsH_3 = (\chi_H - \chi_{As} = 2.1 - 2.0 = 0.1)$

5. Pauling has estimated the approximate percentage of ionic character in various A–B covalent bonds from the ($\chi_A - \chi_B$) values, i.e. electronegativity difference of the two atoms forming the covalent bond.

$\chi_A - \chi_B$	Percentage of ionic character	Nature of A–B bond
0	0	Purely covalent
0.1 to 0.8	0.5–15	Covalent
0.9 to 1.6	19–47	Polar covalent
1.7	50	50% ionic and 50% covalent
1.8 to 3.2	55–93	Ionic

6. Hanny and Smith gave the following equation for calculating the percentage of ionic character in A–B bond on the basis of the values of electronegativity of the atoms A and B.

   Percent of ionic character = $[16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2]$

   This equation gives approximate calculation of percentage of ionic character, e.g. 50% ionic character corresponds to ($\chi_A \sim \chi_B$) equal to 2.1.
7. ($\chi_O - \chi_A$) difference predicts the nature of the oxides formed by the element A. χ_O is the EN of oxygen.

   a. If ($\chi_O - \chi_A$) is large, the oxide shows basic nature, e.g. Na_2O.

   b. If ($\chi_O - \chi_A$) is small, the oxide shows acidic nature, e.g. SO_2.
8. Ionic compounds having character < 20%, the compounds were found to be coloured, e.g.

Compound ⇒	AgCl	AgBr	AgI	Ag_2S
% ionic character ⇒	22%	18%	11%	8%
Colour ⇒	White or colourless	Yellow	Dark yellow	Black

Lesser the percentage of ionic character, darker will be the colour.

ILLUSTRATION 1.47

Calculate the percentage of ionic character in Cs–Cl bond in CsCl molecule. The electronegativity values of Cs and Cl are 0.7 and 3.0 respectively.

Sol. $\chi_A - \chi_B = \chi_{Cl} - \chi_{Cs} = (3.0 - 0.7) = 2.3$

Percentage of ionic character in Cs–Cl bond

$= [16 \times 2.3 + 3.5 \times (2.3)^2] = (36.8 + 18.51) = 55.31$

ILLUSTRATION 1.48

Arrange the molecules, HF, HCl, HBr and HI in the decreasing order of the percentage of ionic character. Electronegativity values are as follows:

H = 2.1 F = 4.0. Cl = 3.0. Br = 2.8. I = 2.5

Sol. Percentage of ionic character in H–F

$(\chi_F - \chi_H) = 4.0 - 2.1 = 1.9$
$= [16 \times 1.9 + 3.5 \times (1.9)^2] = 43$

% ionic character in H–Cl

$(\chi_{Cl} - \chi_H) = 3.0 - 2.1 = 0.9$
$= [16 \times 0.9 + 3.5 \times (0.9)^2] = 17.2$

% of ionic character in HBr

$(\chi_{Br} - \chi_H) = 2.8 - 2.1 = 0.7$
$= [16 \times 0.7 + 3.5 \times (0.7)^2] = 12.9$

% ionic character in HI

$(\chi_I - \chi_H) = 2.5 - 2.1 = 0.4$
$= [16 \times 0.4 + 3.5 \times (0.4)^2] = 7.0$

% of ionic character = HF > HCl > HBr > HI

1.15.4.5 Scales of EN (Measurement of EN)

A number of scales have been developed to measure EN of the atoms. These scales are arbitrary and are based on various types of experimental data such as bond energy, dipole moment, IE and EA. Some of them are explained below:

1. **Pauling scale (1932):** This scale gives a **dimensionless** quantity, commonly referred to as the **Pauling scale**, on a relative scale running from around 0.7 to 3.98 (hydrogen = 2.20). This scale is based on an emporical relation between the bond energy and EN of the two atoms bonded together (A–B) is given by the relation.

   The difference in EN between atoms A and B is given by

$$(\chi_A - \chi_B) = (\text{eV})^{-1/2}\sqrt{E_{A-B} - \frac{1}{2}[E_{A-A} + E_{B-B}]} \quad \text{...(1.2)}$$

Note: 1 eV atom^{-1} = 23.06 kcal mol^{-1}

$$\therefore \quad (23.06)^{-1/2} = \frac{1}{(23.06)^{1/2}} = 0.208$$

Therefore, changing the value of eV in kcal mol^{-1}, Eq. (1.2) becomes

$$(\chi_A - \chi_B) = 0.208\sqrt{E_{A-B} - \frac{1}{2}[E_{A-A} + E_{B-B}]} \text{ kcal mol}^{-1} \quad \text{...(1.3)}$$

Another form of the equation can be written as

$$(\chi_A - \chi_B) = (\text{eV})^{-1/2}\left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}\right]^{\frac{1}{2}} \text{ kcal mol}^{-1} \quad \text{...(1.4)}$$

$$= 0.208\left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}\right]^{\frac{1}{2}} \quad \text{...(1.5)}$$

where χ_A and χ_B are the EN's of two atoms A and B and E_{A-B}, E_{A-A} and E_{B-B} are bond energies of molecules A – B, A_2 and B_2 respectively in kcal mol^{-1}.

In Eqs. (1.4) and (1.5), $[E_{A-B} - \sqrt{(E_{A-A} \times E_{B-B}}]$ is known as **ionic resonance energy** of A–B bond and is denoted by Δ_{A-B}. Thus,

$$\Delta_{A-B} = [E_{A-B} - \sqrt{(E_{A-A} \times E_{B-B}}]$$

Substituting the value of Δ_{A-B} in Eq. (1.4), we get

$$(\chi_A - \chi_B) = 0.208\sqrt{\Delta_{A-B}} \text{ in kcal mol}^{-1} \quad \text{...(1.6)}$$

Note: Converting the value of eV atom^{-1} into kJ mol^{-1} (SI) unit, we know

1 eV atom^{-1} = 96.49 kJ mol^{-1}

$$\therefore \quad (\text{eV})^{-1/2} = \frac{1}{(96.49)^{1/2}} = 0.017$$

Therefore, substituting the value of eV atom^{-1} into kJ mol^{-1} in Eq. (1.2) and (1.4).

From Eq. (1.2), we get

$$(\chi_A - \chi_B) = 0.107\sqrt{E_{A-B} - \frac{1}{2}[E_{A-A} + E_{B-B}]} \text{ kJ mol}^{-1} \quad \text{...(1.7)}$$

From Eq. (1.4), we get

$$(\chi_A - \chi_B) = 0.107\left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}\right]^{\frac{1}{2}} \text{ kJ mol}^{-1} \quad \text{...(1.8)}$$

$$= 0.107\sqrt{\Delta_{A-B}} \text{ kJ mol}^{-1} \quad \text{...(1.9)}$$

Equations (1.7), (1.8) and (1.9) in kJ mol^{-1} can be used and they give approximately the same result.

Note: The dissociation energies of the A–B, A–A and B–B bonds are expressed in eVs, the factor (eV)$^{-1/2}$ is included to ensure a dimensionless result.

2. **Mulliken's scale (1934):**

   a. Mulliken proposed that EN of an atom is equal to the average of its ionisation potential (IP) and electron affinity (EA) values, when IP and EA of the atom are in eV atom^{-1}.

$$\chi_A = \frac{(\text{IP})_A + (\text{EA})_A}{2} \quad \text{...(1.10)}$$

   If the values of IP and EA are taken in kcal mol^{-1}, then

$$\chi_A = \frac{(\text{IP})_A + (\text{EA})_A}{2 \times 62.5} = \frac{(\text{IP})_A + (\text{EA})_A}{125} \quad \text{...(1.11)}$$

   If the value of IP and EA are taken in kJ mol^{-1}, then

$$\chi_A = \frac{(\text{IP})_A + (\text{EA})_A}{540} \quad \text{...(1.12)}$$

   Alternatively: However, it is more usual to use a linear transformation to transform these absolute values into values which resemble the more familiar Pauling values. For IP and EA in eV,

$$\chi_A = 0.187\,(\text{IP} + \text{EA}) + 0.17 \quad \text{...(1.13)}$$

   and for IP and EA in kJ mol^{-1},

$$\chi_A = (1.97 \times 10^{-3})\,(\text{IP} + \text{EA}) + 0.19 \quad \text{...(1.14)}$$

   b. Mulliken's values of EN are about 2.8 times more than the Pauling's values. Hence to make the Mulliken's values approximately equal to the Pauling's values, then Eq. (1.11) becomes

$$\chi_{Pauling} = \frac{(IP)_A + (EA)_A}{2 \times 2.8} = \frac{(IP)_A + (EA)_A}{5.6} \quad ...(1.15)$$

OR

$$\chi_{Pauling} = \frac{\chi_{Mulliken}}{2.8} \quad ...(1.16)$$

The constant 1/56 is called scale adjustment factor. This factor is used when IP and EA are taken in eV.

c. In terms of electron gain enthalpy ($\Delta_{eg}H^{\ominus}$), Mulliken scale can be written as

$$\chi_A = \left[\frac{\Delta_i H^{\ominus} - \Delta_{eg}H^{\ominus}}{2}\right]$$

where $\Delta_i H^{\ominus}$ represents ionisation energy.

d. The Mulliken EN values are scaled down to match the Pauling values by dividing $\left(\frac{IP + EA}{2}\right)$ in eV by 3.17

The Mulliken EN can only be calculated for an element for which EA is known. The Mulliken EN of an atom is sometimes said to be the negative of the chemical potential. By inserting the energetic definitions of the IP and EA into the Mulliken EN, it is possible to show that the Mulliken chemical potential (μ_M) is a finite difference approximation of electronic energy with respect to the number of electrons, i.e.

$$\mu_M = -\chi_M = \frac{-(IP + EA)}{2}$$

3. **Allred–Rochow's scale (1958):** This scale is based on covalent radii. According to this scale, EN of an atom is the force of attraction between the nucleus of one atom and an electron of an adjacent atom bonded to it and separated from the nucleus by the covalent radius. Thus,

$$\text{EN or } (\chi_A) = 0.359 \times \frac{Z_{eff}}{r^2} + 0.744 \quad ...(1.17)$$

where r is the radius of an atom in angstrom units (A°). The value of Z_{eff} is calculated on the basis of Slater's rule taking all the electrons.

ILLUSTRATION 1.49

The ionic resonance energy of C–H bond is ≈ 6.0 kcal mol^{-1}. The EN of H is 2.1. Calculate EN of carbon ?
Given: $\Delta_{C-H} \approx 6.0$ kcal mol^{-1}

Sol. $(\chi_C - \chi_H) = 0.208\left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}\right]^{\frac{1}{2}}$

$$= 0.208 \times (\Delta_{C-H})^{\frac{1}{2}}$$

$$= 0.208 \times (6.0)^{\frac{1}{2}} = 0.208 \times 2.5 = 0.52$$

$$\chi_C - \chi_H = 0.52$$

$$\therefore \quad \chi_C = 0.52 + 2.1 = 2.62$$

1.15.4.6 Bond Strength

If the EN difference of a covalently bonded atom ($\Delta\chi$) increases, the bond energy of the covalent bond also increases. For example, the decreasing order of the H–X bond strength is

H–F > H–Cl > H–Br > H–I

As the bond strength is decreasing the acid strength is increasing. So the other increasing acid strength is

HF < HCl < HBr < HI

1.15.4.7 Acidic and Basic Nature of Oxides of Normal Elements in a Period

1. The acidic nature of the oxides of normal elements increases along the period (→), due to the increase of EN of the elements from the left to the right in a period.
The order of acidic or basic nature of the oxides of the 3rd period is given as under.

Group	1	2	14	15	16	17
	Na_2O	MgO	SiO_2	P_2O_5	SO_3	Cl_2O_7

$\longrightarrow$
Acidic nature is increasing
$\longleftarrow$
Basic nature is decreasing

2. **Acidic and basic character of XOH molecule in aqueous solution:** Whether a given compound of XOH type (X = metal or non-metal) will behave as an acid or a base in aqueous solution is explained by considering the ionisation of XOH molecule in aqueous solution as follows:

a. If $\chi_O - \chi_H > \chi_O - \chi_x$; then O–H bond will be more polar than O-X bond and hence the ionisation of XOH molecule in aqueous solution will take place at O–H bond and $H_3O^{\oplus}$ ions will be formed, as shown:

$$X{-}O \vdots H + H_2O \rightarrow XO^{\ominus} + H_3O^{\oplus}$$

The formation of $H_3O^{\oplus}$ shows that XOH will behave as an acid in its aqueous solution.

b. If $\chi_O - \chi_H < \chi_O - \chi_x$, then X–O bond will be more polar than O–H bond and hence the ionisation of XOH molecule in aqueous solution will take place at X–O bond and $\overset{\ominus}{O}H$ ions will be formed as shown:

$$X \vdots OH \longrightarrow X^{\oplus} + \overset{\ominus}{O}H$$

$$X^{\oplus} + H_2O \longrightarrow [X(OH_2)]^{\oplus}$$

$$XOH + H_2O \longrightarrow [X(OH_2)]^{\oplus} + \overset{\ominus}{O}H$$

The formation of $\overset{\ominus}{O}H$ ions shows that XOH will behave as a base in its aqueous solution.

c. From the above discussion it is evident that hydroxy compounds of metals such as groups 1 and 2 behave as bases in aqueous solution (except Be $(OH)_2$, which is amphoteric in nature) while those of non-metals like halogens behave as acids (see Illustration 1.51).

ILLUSTRATION 1.50

Arrange the following compounds in order of their decreasing stabilities:
HF, CCl_3, HBr, HI, HCl.
(Given EN values of elements as below)
H = 2.1, F = 4, Cl = 3.0, Br = 2.8, I = 2.3, N = 3.0

Sol. EN differences for:

$HF = 4.0 - 2.1 = 1.9$, $NCl_3 = 3.0 - 3.0 = 0.0$
$HBr = 2.8 - 2.1 = 0.7$, $HI = 2.3 - 2.1 = 0.2$
$HCl = 3.0 - 2.1 = 0.9$.

The greater the differences in EN, the greater is the bond energy of the covalent bond and the greater is the stability of the covalent bond.

So, the order of decreasing stability is

$$\begin{Bmatrix} \begin{bmatrix}\text{Compound} \\ \Delta\chi\end{bmatrix} & \begin{matrix} : HF > HCl > HBr > HI > NCl_3 \\ :1.9 \quad 0.9 \quad 0.7 \quad 0.4 \quad 0.0 \end{matrix} \end{Bmatrix}$$

ILLUSTRATION 1.51

Predict which of the following hydroxy compounds is acidic and which is basic in aqueous solution:
i. CsOH ii. IOH.
EN values are: Cs = 0.7, O = 3.5, H = 2.1, I = 2.5.

Sol. The EN values of different elements present in CsOH and IOH and those of $\chi_O - \chi_H$, $\chi_O - \chi_{Cs}$ and $\chi_O - \chi_I$ are given below:

$$\begin{Bmatrix} \Delta\chi \Rightarrow & Cs & \overset{2.8}{\text{———}} & O & \overset{1.4}{\text{———}} & H \\ EN \Rightarrow & 0.7 & & 3.5 & & 2.1 \end{Bmatrix} \quad \begin{matrix} I & \overset{1.0}{\text{———}} & O & \overset{1.4}{\text{———}} & H \\ 2.5 & & 3.5 & & 2.1 \end{matrix}$$

Here $\chi_O - \chi_{Cs}$ (2.8) > $\chi_O - \chi_I$ (1.0), so CsOH will give $\overset{\ominus}{O}H$ ions while IOH will give $H_3O^{\oplus}$ ions, consequently CsOH behaves as a base while IOH behaves as an acid.

ILLUSTRATION 1.52

NaOH behaves as a base while $Zn(OH)_2$ is amphoteric. Why?

Sol. In $Na \vdots O - H$, $\chi_O - \chi_{Na} > \chi_O - \chi_H$, therefore it is the Na–O bond breaks and releases $\overset{\ominus}{O}H$ ions. So, NaOH is basic.

But in $Zn \vdots O \vdots H$, $\chi_O - \chi_{Zn} = \chi_O - \chi_H$, therefore there is equal probability that the bond breaks in both ways (releasing both $H_3O^{\oplus}$ and $\overset{\ominus}{O}H$ in aqueous solution). So, $Zn(OH)_2$ is amphoteric.

1.15.5 Differences Between $\Delta_{eg}H^{\ominus}$ and EN

These are summarised below:

$\Delta_{eg}H^{\ominus}$	EN
1. It is the tendency of an isolated gaseous atom to attract an electron.	1. It is the tendency of an atom in a molecule to attract the shared pair of electrons.
2. It can be measured experimentally and is usually expressed in eV atom^{-1} or kJ mol^{-1}.	2. It cannot be measured experimentally. It is only a relative number with respect to F taken as 4.0.
3. $\Delta_{eg}H^{\ominus}$ of an atom is constant.	3. EN of an atom is not constant. It depends on the state of hybridisation of the atom, e.g. EN of sp hybridised atom > sp^2 hybridised atom > sp^3 hybridised atom. It also depends on oxidation state (OS) of an element. EN $\propto$ OS. It also depends on the nature of substitutent attached to it. EN of C in CF_3Br > EN of C in CH_3Br.
4. It is the property of an isolated atom.	4. It is property of bonded atom.
5. It does not change regularly in a period or group.	5. It changes regularly in a period and there are certain exception in a group.

1.16 SOME IMPORTANT BOND CHARACTERISTICS

1. **Bond length:** The equilibrium distance between the centres of the nuclei of the two bonded atoms is called its bond length.

   It is expressed in terms of Angstrom (1A° = 10^{-10} m) or picometer (1 pm = 10^{-12} m). It is determined experimentally by the X-ray diffraction or electron diffraction methods or spectroscopic methods.

   a. **Factors affecting bond length:**

   i. **Size of the atoms:** Bond length increases with the increase in the size of the atoms, e.g. bond lengths of H–X are in the order as H–I > H–Br > H–Cl > H–F.

   ii. **Multiplicity of bond:** The bond length decreases with multiplicity of bond, i.e.

   bond length of $C \equiv C < C = C < C - C$.

   iii. **Types of hybridisation:** Since s-orbital is smaller is size, the greater the s-character, the shorter is the hybrid orbitals and hence shorter is the bond length, e.g. bond lengths of sp^3, sp^2 and sp hybrid orbitals of C–H bond are in the order as:

   sp^3 (C–H) > sp^2 (C–H) > sp (C–H).

   b. **Calculation of bond length:** Generally in case of heteroatomic molecule of AB type, bond length, $d_{(A-B)}$ is equal to the sum of covalent radii of A and B atoms

   $$d_{(A-B)} = r_A + r_B \quad \text{...(1.18)}$$

Although Eq. (1.18) holds good in most of the heteroatomic molecules, yet the experimental value of $d_{(A-B)}$ is found to be slightly less than the sum of r_A and r_B. The decrease in bond length is due to the ionic character in A–B bond. The increase in ionic character of A–B bond decreases the bond length, $d_{(A-B)}$.

Schomarkar and Stevenson (1941) proposed the following formula for the calculation of bond length.

$$d_{(A-B)} = r_A + r_B - 0.09\,(\chi_A - \chi_B) \qquad ...(1.19)$$

(χ_A and χ_B are the EN's of A and B elements.)

$$\therefore\ d_{(A-B)} \propto \frac{1}{(\chi_A - \chi_B)} \propto \text{Stability of AB molecule} \qquad ...(1.20)$$

i.e. lesser is the value of $(\chi_A - \chi_B)$, more will be the bond length and thus less will be the stability of AB molecule.

ILLUSTRATION 1.53

Calculate the $d_{(N-C)}$ in $(CH_3)_3N$ molecule by using Eqs. (1.18) and (1.19) above and show from which equation $d_{(N-C)}$ closely resembles with the experimental value of $d_{(N-C)} = 1.47$ Å.

Given: $r_N = 0.75$ Å, $r_C = 0.77$ Å, $\chi_A = 3.0$, $\chi_C = 2.5$

Sol. Using Eq. (1.18), we get

$$d_{(N-C)} = r_N + r_C = (0.75 + 0.77)\text{ Å} = 1.52\text{ Å}$$

Using Eq. (1.19), we get

$$\begin{aligned} d_{(N-C)} &= r_N + r_C - 0.09\,(\chi_N - \chi_C) \\ &= 0.75 + 0.77 - 0.09\,(3.0 - 2.5) \\ &= 1.475\text{ Å} \end{aligned}$$

The value of $d_{(N-C)}$ closely resembles the experimental value by using Eq. (1.19).

2. **Bond strength or bond energy or bond enthalpy:** It is the amount of energy required to break one mole of bonds of a particular type so as to separate them into gaseous atoms. It is expressed in kJ mol^{-1}.

   a. **Factors affecting bond strength:**

      i. **Size of the atoms:** The greater the size of the atoms, the greater is the bond length and less is the bond dissociation energy or bond strength.

      ii. **Multiplicity of bonds:** The bond strength increases with the multiplicity of the bond, e.g. bond dissociation energy are in the order:

      $N \equiv N > O = O > H - H.$

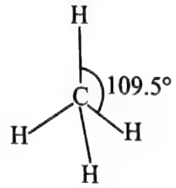
      iii. **Number of lone pairs of electrons present:** The greater is the number of lone pairs of electrons present on the bonded atoms, the greater is the repulsion between the atoms and hence the less is the bond dissociation energy.

3. **Bond angle:** A bond is formed by the overlap of atomic orbitals. The direction of an overlap gives the direction of the bond.

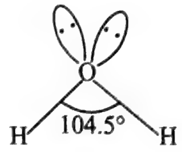
The angle between the lines representing the direction of the bonds, i.e. the orbitals containing the bonding electrons, is called the bond angle

Alternatively: It is the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion.

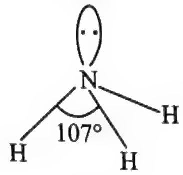
It is expressed in degree, minutes and second. For example, H–C–H bond angle in CH_4, H–O–H bond angle in H_2O, H–N–H bond angle in NH_3 and Cl–B–Cl bond angle in BCl_3 are shown as:



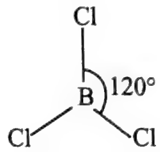
(CH_4)



(H_2O)



(NH_3)



(BCl_3)

a. **Calculation of bond angles:**

   i. The concept of EN has been found to be very useful to explain the variation of bond angle.

   For example, for AB_x type molecule (A is the central atom, B are the atoms attached with atom A and x is the number of B atoms), the B–A–B bond angle is changed with the change of EN of central atom or with change of size of central atom

Rule (i): If the EN of central atom decreases or/and size increases bond angle decreases.

$$\text{Bond angle (B–A–B)} \propto \text{EN of central atoms and} \propto \frac{1}{\text{Size of central atom}}$$

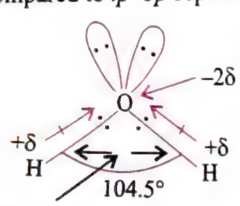
Table 1.13 Change of bond angle of hydrides of groups 15 and 16 with change of EN and size of central atom

(Hydrides of group 15) (A = N, P, As, Sb)	EN of central atom A	H–A–H bond angle	
NH_3	N = 3.0	H–N–H = 107.5°	Bond angle decreases as EN of central atom decreases or size of central atom increases ↓
PH_3	P = 2.1	H–P–H = 93.3°	
AsH_3	As = 2.0	H–As–H = 91.8°	
SbH_3	Sb = 1.9	H–Sb–H = 91.3°	
Decreasing order of EN of central atom A: N > P > As > Sb. Increasing order of size of central atom A: N < P < As < Sb.			

(Hydrides of group 16) A = O, S, Se, Te	EN of central atom A	H–A–H bond angle	
H_2O	O = 3.5	H–O–H = 104.5°	Bond angle decreases as EN of central atom decreases or size of A increases ↓
H_2S	S = 2.5	H–S–H = 92.3°	
H_2Se	Se = 2.4	H–Se–H = 91°	
H_2Te.	Te = 2.1	H–Te–H = 90°	
Decreasing order of EN of central atom A: O > S > Se > Te Increasing order of size of central atom A: O < S < Se < Te			

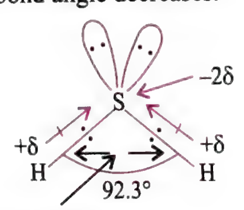
Explanation: For example, the angle of $H_2O > H_2S$ (Figs. 1.10(a) and 1.10(b)).

The outer shell electronic configuration of group 16 elements is $ns^2\ np^4$ or $ns^2\ np_x^2\ np_y^1\ np_z^1$. They undergo sp^3 hybridisation, containing 2 lone pairs The expected bond angle is 109°, 28′. But due to greater *lp–lp* repulsion as compared to *lp–bp* repulsion, bond angle decreases.



Smaller distance (closer bond pairs), more repulsion.

Fig. 1.10(a)



Larger distance (farther bond pairs), lesser repulsion

Fig. 1.10(b)

Note: Charge – 2δ on O > Charge – 2δ on S.
Similarly charge +δ on H in NH_3 > charge +δ on H in H_2S.

ii. **Effect of EN:** As O-atom has higher EN than S atom, O–H bond is sufficiently polar i.e. there is a significant more positive charge (+δ) on H-atoms in H_2O than on H-atoms in H_2S. So, there is greater repulsion between H-atoms in H_2O and H_2S.

Hence H–O–H bond angle > H–S–H bond angle.

iii. **Effect of size:** O-atom is smaller in size than S-atom. So, the bond length of (O–H) in H_2O is less than the bond length of (S–H) in H_2S. As a result H-atoms in H_2O are quite close so that they repel each other and the bond angle (H–O–H) increases to 104.5° and the bond angle (H–S–H) decreases to 92.3°.

Alternatively: With the decrease of EN from O (3.5) to Te (2.1), the A–H bonding electron pairs in AH_3 molecules are drawn farther away from the central atom (A) but nearer to H-atom. The effect of this shifting of bonding electron paris (*bp*) towards H-atom is that the repulsion between the bonding electron pairs (*bp*) and lone pairs (*lp*) on central atom [(*bp–lp*) repulsion] increases. The increase in (*bp–lp*) repulsion results in that bonding electron pair come still close to each other and hence the bond angle progressively decreases from H_2O to H_2Te.

Similarly, the decrease in bond angle of the hydrides of group 15 can also be explained.

iv. For AB_x type molecule, the B–A–B bond angle is changed with the change of EN of atom B.

Rule (ii): If the EN of atom B decreases, the bond angle (B–A–B) increases.

$$\text{Bond angle (B–A–B)} \propto \frac{1}{\text{EN of atom B}}.$$

This is evident from the data given in Table 1.14.

Table 1.14 Change of bond angle of AB_x molecules with the change of EN of atom B

	AB_x molecules	EN of B atom	B–A–B angle
1.	PF_3	4.0	≈ 98.5°
2.	PCl_3	3.0	100°
3.	PBr_3	2.8	101.5°
4.	PI_3	2.5	102
5.	AsF_3	4.0	≈ 90.0°
6.	$AsCl_3$	3.0	98.4°
7.	$As\ Br_3$	2.8	100.5°
8.	$As\ I_3$	2.5	101.5°
9.	NF_3	4.0	102°
10.	NH_3	2.1	107°
11.	OF_2	4.0	103°
12.	OH_2	2.1	104.5°

Explanation: The decrease in bond angle, with increase of EN of atom B, the electron pair is attracted more towards more EN atom B, so the bond pairs of electron are away from central atom A or in other words, the distance between bond pairs is more. As a result the repulsion between the bond pairs in AB_x molecule (with more EN of atom B) is less and the bond angle is less.

For example, bond angle of $NH_3 > NF_3$ [see Figs. 1.11(a) and 1.11(b)].

Both NH_3 and NF_3 are pyramidal in shape with one lone pair on N. Since the EN of F > EN of H, the electron pair is attracted more towards F in NF_3, i.e. bond paris of electrons are away from N or in other words, the distance between bond pairs is more. As a result, the repulsion between the bond pairs in NF_3 is less than in NH_3.

Due to the greater repulsion between the bond pairs in NH_3 than in NF_3, the bond angle in NH_3 (107°) is greater than that in NF_3 (102°).

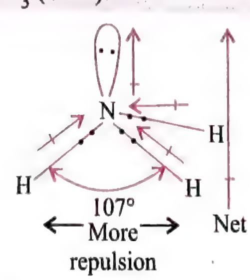


Fig. 1.11(a) NH_3 molecule

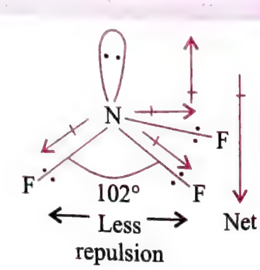
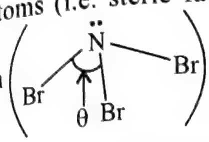


Fig. 1.11(b) NF_3 molcules

Exception: (i) Bond angle of $NBr_3 > NH_3$
(ii) Bond angle of $NMe_3 > NH_3$

i. Expected bond angle of NH_3 should be greater than NBr_3 but observed bond angle is $NBr_3 > NH_3$.
According to Rule (ii), if the EN of atom B decreases, the bond angle increases (EN of H = 2.1, EN of Br = 2.8).
Since size of Br-atom is very large in comparison to the size of H-atom, so due to repulsion between Br atoms (i.e. steric factor), the bond angle Br–N–Br in



increases.

ii. Similarly, expected bond angle of NH_3 should be greater than NMe_3 but observed bond angle is $NMe_3 > NH_3$.
Same explanation as in (i), that is due to steric factor.

Rule iii: Molecules or ions without non-bonding electrons on central atom and having regular geometry, the change in EN of the central atom or the surrounding atom has no effect on the bond angle.

For example, BF_3, BCl_3, BBr_3, etc. all have the same bond angle of 120°. Similarly, CH_4, CBr_4, CCl_4, $\overset{\oplus}{N}H_4$, etc., have the same bond angle of 109°, 28′.

Rule iv: For the molecule with same central atom with vacant *d*-orbitals, and with different B atom, the bond angle increases with the increase of EN of B atom having lone pairs of electrons.

Explanation: For example, bond angle of $PF_3 > PH_3$ (opposite to NH_3 and NF_3) (opposite of Rule (ii)).
This is due to back bonding or ($p\pi$–$d\pi$) multiple bond character. Due to this, PF_3 molecule shows resonance leading to partial bond character as shown in Figs. 1.12 and 1.13.

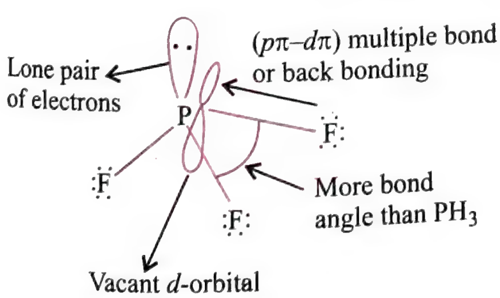
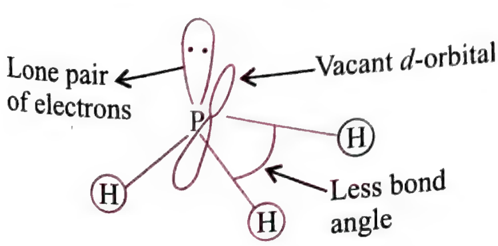


Fig. 1.12 (a) PF_3 molecule



(Here H-atoms do not have lone pair of electrons for the formation of $p\pi$–$d\pi$ bond)

Fig. 1.12 (b) PH_3 molecule

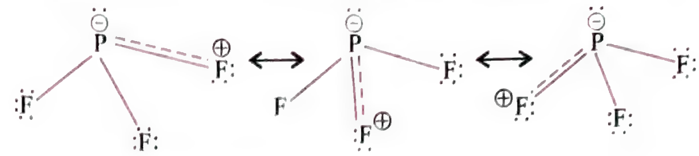


Fig. 1.13 Resonance structures of PF_3 molecule

Due to this, the repulsion between P and F bonds is large and hence the bond angle is large. There is no possibility for the formation of double bonds in PH_3, although P-atoms have vaccant *d*-orbitals but H-atom does not have lone pair of electron for back donation or for the formation of ($p\pi$–$d\pi$) multiple bond.

v. State of hybridisation:

Rule v: State of hybridisation (sp, sp^2, sp^3) is also used to determine the bond angle, since sp, sp^2 and sp^3 hybridisation have 180°, 120° and 109° 28′ bond angle respectively.

For example, the bond angle of
$\overset{\oplus}{N}O_2\,(180°) > NO_2\,(134°) > NO_3^{\ominus}(120°) > NO_2^{\ominus}\,(115°)$

Explanation:

- $\overset{\oplus}{\mathbf{N}}\mathbf{O_2}$**:** It has *sp* hybridisation with bond angle of 180°, as shown below:

Ist formula:

Hybridisation $(H) = \frac{1}{2}\,(V + M - \text{number of +ve charge})$

where V = number of valence e^-'s (For N = $2s^2\,2p^3$,
$\therefore\ V = 5e^-$)

M = number of monovalent atom attached to central atom = zero.

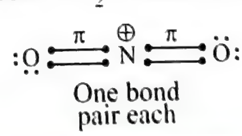
$$\therefore \qquad H = \frac{1}{2}\,(5 + 0 - 1) = 2 = sp$$

Alternatively:

H = Number of bond pairs (bp) + Number of lone pairs (lp)
OR
= Number of bond pairs (bp) + Number of odd electrons (one unshared e^-)

$\therefore\ H = 2 + 0 = 2 = sp$

Hence the shape of $\overset{\oplus}{N}O_2$ is linear with bond angle of 180°.



Note: π bond is excluded in bond pairs

$\mathbf{NO_2}$**:** It has sp^2 hybridisation with expected angle of 120° but observed angle is 134°.

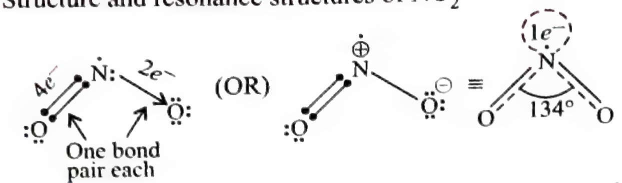
Hybridisation = Number of bond pairs + Number of odd $\bar{e}$ s
$= 2 + 1 = 3 = sp^2$

OR

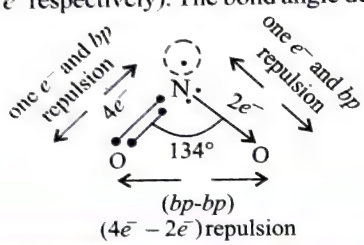
Hybridisation $= \frac{1}{2}\,(V + M + \text{Number of odd } \bar{e} \text{ s})$

$$= \frac{1}{2}\,(5 + 0 + 1) = 3 = sp^2$$

Structure and resonance structures of NO_2



Due to *bp–bp* repulsion ($4e^-$–$2e^-$ repulsion), the bond angle is slightly increased from 120° to somewhat greater than 134°. But there is also a repulsion between one odd electron (or one unshared e^- or one non-bonding e^-) and the *bp* (i.e. $4e^-$ and $1e^-$ respectively). The bond angle decreases to 134°.

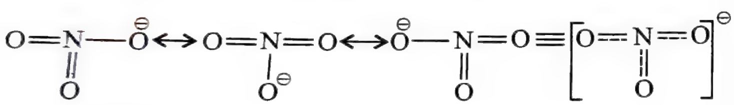


Note: (one e⁻ – bp) repulsion > (bp – bp) repulsion.

$NO_3^{\ominus}$: It is sp^2 hybridised with bond angle of 120°. It shows three resonating structures.

$$H = \frac{1}{2}\,(V + M + \text{number of} - \text{ve charge})$$

$$= \frac{1}{2}\,(5 + 0 + 1) = 3 = sp^2 \text{ hybrid}$$

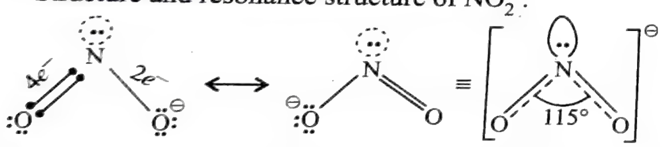


$NO_2^{\ominus}$: It is sp^2 hybridised with expected bond angle of 120° but observed angle is 115°.

$$H = \frac{1}{2}\,(V + M + \text{number of} - \text{ve charge})$$

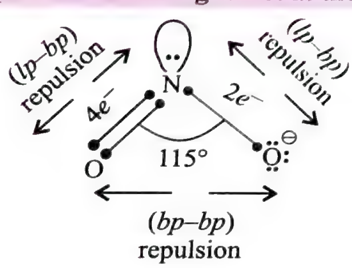
$$= \frac{1}{2}\,(5 + 0 + 1) = 3 = sp^2 \text{ hybrid}$$

Structure and resonance structure of $NO_2^{\ominus}$.



Due to *bp–bp* repulsion ($4e^-$–$2e^-$ repulsion), bond angle is slightly increased from 120° to somewhat greater 120°. But there is also repulsion between *lp* and *bp*, which decreases the bond angle to 115°.

Note: Here (lp–bp) repulsion >> (bp–bp) repulsion and also, as in case of NO_2,
(lp–bp) repulsion > (one e⁻–bp) repulsion.
This repulsion produces **bending effect** in the molecule.



Comparison of bond angle of NO_2 and $NO_2^{\ominus}$: NO_2 h one non-bonding (or one unshared e^-) whereas $NO_2^{\ominus}$ has one lone pair of electrons (or two non-bondi e^-'s). Hence, (*lp–bp*) repulsion in $NO_2^{\ominus}$ is greater th (one e^-–*bp*) repulsion in NO_2, hence repulsion on the bo pairs is more and the bond angle is less in $NO_2^{\ominus}$ as compar to bond angle in NO_2.

Note:

i. $NO_2^{\oplus}$ is *sp* hybridised and linear, bond angle is 180°.

ii. NO_2 is bent, due to (one e⁻–bp) repulsion, bond angle i 134°.

iii. $NO_3^{\ominus}$ is sp^2 hybridised and planar, bond angle is 120°.

iv. $NO_2^{\ominus}$ is bent, due to (lp–bp) repulsion, bond angle is 115°

Therefore, decreasing order of bond angle is

$NO_2^{\oplus} > NO_2 > NO_3^{\ominus} > NO_2^{\ominus}$

ILLUSTRATION 1.54

I. In which of the following triatomic molecules, the observed bond angle is 116°, 49′?

a. H_2O b. OF_2 c. CO_2 d. O_3

II. In which of the following molecules, bond angle is the maximum?

a. $BeCl_2$ b. H_2O c. H_2S d. CH_4

III. In which of the following molecules, bond angle between two adjacent covalent bonds is smallest?

a. Be H_2 b. BF_3 c. NH_3 d. CCl_4

IV. Bond angle (H—S—H) in H_2S is close to

a. 109° b. 107° c. 105° d. 90°

V. The hybridisation of B in BF_3 is sp^2. The bond angle in $BF_4^{\ominus}$ will be

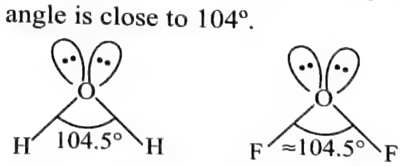
a. 107° b. 109° c. 120° d. 180°

VI. Which of the following molecules contains a bond angle which is smaller than the bond angle in CH_4?

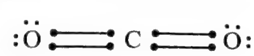
a. SF_6 b. SO_2 c. O_3 d. $\overset{\oplus}{N}H_4$

Sol. **I. (d)**

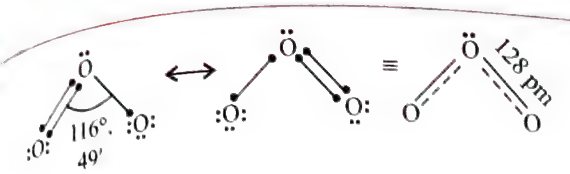
For (a) and (b): $H_2\ddot{O}$ and $\ddot{O}F_2$ both are bent molecules in which O-atom is sp^3 hybridised. Due to (*lp–lp*), (*lp–bp*) and (*bp–bp*) repulsion, the bond angle is close to 104°.



c. In CO_2, C is *sp* hybridised and it is linear molecule with bond angle of 180°.

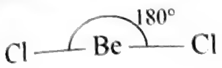


d. Only in O_3, bond angle is close to 116° 49′, because the central O atom is sp^2 hybridised. Hence the answer is (d).



II (a)

a. In $BeCl_2$, Be is sp hybridised and it is linear molecule so the bond angle is = 180°.



b. In $H_2\ddot{O}$:, O is sp^3 hybridised and due to repulsion between (lp–lp), (lp–bp) and (bp–bp), the bond angle is 104.5°.

c. In $H_2\ddot{S}$:, S is sp^3 hybridised but according to rule (i), the bond angle is 92.3°.

d. In CH_4, C is sp^3 hybridised, since there is no lone pair of electrons, thus only (bp–bp) repulsions. Hence the bond angle is 109° 28′.

Thus the answer is (a).

III (c)

a. BeH_2 is linear, the bond angle is 180°.

b. BF_3 is trigonal planar, the bond angle is 120°.

c. In $\ddot{N}H_3$, N is sp^3 hybridised and due to greater repulsion between (lp–bp) and (bp–bp) the bond angle is reduced to 107°.

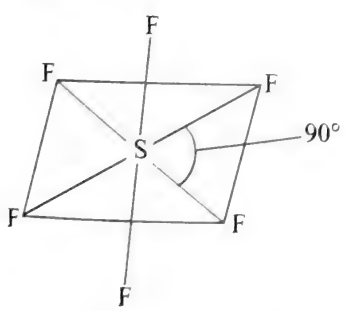
d. In CCl_4, C is sp^3 hybridised, the bond angle is 109°28′ as explained above for CH_4.

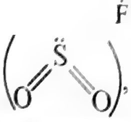
IV (d): Refer to Section 1.16, Point 3(a).

V (b): In $BF_4^{\ominus}$, B is sp^3 hybridised and the bond angle is 109°28′.

VI (a)

a. In SF_6, S is sp^3d^2 hybridised having octahedral shape, each bond angle is 90°.



b. In $\ddot{S}O_2$ , S is sp^2 hybridised but due to greater repulsion between (lp–bp) and (bp–bp), the angle is reduced to 118°.

c. O_3 is sp^2 hybridised and the bond angle is 116° as explained above in Illustration 1.54 (I) (d).

d. $\overset{\oplus}{N}H_4$ is sp^3 hybridesied, since due to the absence of lone pair electrons on N atom, thus only (bp–bp) repulsions, so bond angle is 109° 28′.

Hence the answer is (a).

1.17 PERIODIC TRENDS IN CHEMICAL PROPERTIES (SOME OTHER PERIODIC PROPERTIES)

Some of the trends in chemical properties of elements are described below.

1.17.1 Periodicity of Valence or Oxidation States

The valence or oxidation state is very important property of elements and can be understood in terms of their electronic configuration.

The electrons present in the outermost shell of an atom are called **valence electrons**, and their numbers determine the valence or valency of the atom.

The valence of the s and p block (representative) elements is usually equal to the number of electrons in the outermost orbitals and/or equal to eight minus the number of the outermost electrons.

However, transition and the inner transition elements show variable valence due to the participation of not only the valence electrons but d- and f-electrons also in the bond formation. But their most common valence are 2 and 3.

1. **Variation of valence in period:** Along the period (→) the number of valence electrons increases from 1 to 18. But the valence of elements, w.r.t. H or O first increases from 1 to 4 and then decreases to zero. These trends are observed in the valence of hydrides and oxides.

   To explain the concept of valence or oxidation state, consider the two compounds containing oxygen, OF_2 and Na_2O.

   The decreasing order of EN of F, O and Na are

   F > O > Na

   Outer electronic configuration of F = $2s^2\ 2p^5$.

   Each of the atom of F shares one electron with oxygen in the OF_2 molecule. Being the highest electronegative element, fluorine is given oxidation state −1. Since there are two fluorine atoms in this molecule, oxygen with the outer electronic configuration $2s^2\ 2p^4$ shares two electrons with fluorine atoms and thereby exhibits oxidation state +2.

   In Na_2O, oxygen being more electronegative accepts two electrons, one from each of the two sodium atoms and, thus, shows oxidation state −2. On the other hand, sodium with electronic configuration $3s^1$ loses one electron to oxygen and is given oxidation state +1.

Thus, the oxidation state of an element in a particular compound can be defined as the charge acquired by its atom on the basis of electronegative consideration from other atoms in the molecule.

2. **Variation of valence in a group:** Down the group (↓), the number of valence electrons remains the same, so all the elements in the same group exhibit the same valence.

ILLUSTRATION 1.55

Using the periodic table, predict the formulas of compounds which might be formed by the following pairs of elements: (a) silicon and bromine (b) aluminium and sulphur.

Sol.

a. Silicon is group 14 element with a valence of 4; bromine belongs to the halogen family with a valence of 1. Hence, the formula of the compound formed would be $SiBr_4$

b. Aluminium belongs to group 13 with a valence of 3; sulphur belongs to group 16 elements with a valence of 2. Hence, the formula of the compound formed would be Al_2S_3.

1.18 TYPICAL ELEMENTS

Elements of **third period** are also called as **typical elements**. These include Na, Mg, Al, Si, P, S, Cl. The properties of all elements belonging to a particular group resemble the properties of the corresponding typical element of that group. For example, the general properties of alkali metal can be predicted from the behaviour of Na, not Li, the first member of the family.

The typical elements (all having $n = 3$) can take up 18 electrons. Note that for these elements $3d$ sub-shell is available but it is not filled, i.e. these have vacant d sub-shell. This is not the case with second period elements, hence they have somewhat different properties than the rest of the group or we can say that it is the typical element, which in true sense represents a group.

1.19 BRIDGE ELEMENTS

Elements of the **IInd period** are also called as **bridge elements**. The properties of these elements resemble the properties of elements of the IIIrd period placed diagonally, as shown.

IInd period	Li	Be	B	C	
IIIrd period	Na	Mg	Al	Si	P
	1	2	3	4	

Number of group = 4
Number of periods = 2
Pairs of elements diagonally placed = 3

1.20 ANOMALOUS PROPERTIES OF THE SECOND PERIOD ELEMENTS (DIAGONAL RELATIONSHIP)

The first element of each of the groups 1 (lithium) and 2 (beryllium) and groups 13–17 (boron to fluorine) differs in many respects from the other members of their respective groups.

For example, lithium unlike other alkali metals, and beryllium unlike other alkaline earth metals, form compounds with significant covalent character, the other members of these groups mainly form ionic compounds. The behaviour of lithium and beryllium is more similar with the second element of the following group, i.e. Mg and Al respectively. This is called **diagonal relationship** in the periodic properties.

Property	**Element**		
Metallic radius (M/pm)	**Li** 152	**Be** 111	**B** 88
	Na 186	**Mg** 160	**Al** 142
Ionic radius ($M^{\oplus}$/pm)	$Li^{\oplus}$ 76	$Be^{\oplus}$ 31	
	$Na^{\oplus}$ 102	$Mg^{\oplus}$ 72	

The anomalous behaviour is due to the

- small size
- high charge density (charge/radius) ratio
- high polarising power [Ionic charge/(Ionic radius)^2]
- high EN of the element

Explanation:

1. Along the period (→), EN of the element increases while down the group (↓) electropositivity of the element increases or EN decreases.

   These two effects tend to cancel each other in moving diagonally from the top left to the bottom right. Therefore the elements diagonally related in this way tend to have similar properties. They form similar compounds though the valency is different. Sometimes the diagonal relationship is explained in terms of polarising power $\left[\dfrac{\text{Ionic charge}}{(\text{Ionic radius})^2}\right]$

   On moving along a period, the charge on the ions increases while ionic size decreases hence polarising power increases. On moving down the group the ionic size increases and hence polarizing power decreases. On moving diagonally these two effects cancel each other to some extent and hence properties remain similar.

2. The first member of the group has only four valence orbitals ($2s$ and $2p$) available for bonding, whereas the second member of the groups has nine valence orbitals ($3s$, $3p$ and $3d$). As a consequence of this, the maximum covalency of the first member of each group is 4, e.g. boron can only form $[BF_4]^{\ominus}$, whereas the other members of the groups can expand their valence shell to accommodate more than four pairs of electrons, e.g. aluminium forms $[AlF_6]^{3-}$.

3. Because of the smaller size and the higher EN, the first member of p-block elements displays greater ability to form $p\pi$–$p\pi$ multiple bonds to itself (e.g. C=C, C≡C, N=N, N≡N) and to the other second period elements (e.g. C=O, C=N, C≡N, N=O) compared to subsequent members of the same group.

Note: Diagonal relationship between (i) Li and Mg is due to same charge density (ii) between Be and Al is due to same charge density and EN (iii) between B and Si is due to same size, EN and IE.

1.20.1 Diagonal Relationship Between Lithium and Magnesium (Chemical Properties)

As an illustration, let us consider diagonal relationship between lithium and magnesium.

1. Ionic radius of $Li^{\oplus}$ is 0.60 Å and that of Mg^{2+} is 0.65 Å.
2. Li and Mg react with oxygen to form normal oxides.

$$4Li + O_2 \longrightarrow 2Li_2O$$
$$2Mg + O_2 \longrightarrow 2MgO$$

3. Both of them react with nitrogen to form nitrides, Li_3N and Mg_3N_2

$$6Li + N_2 \longrightarrow 2Li_3N \xrightarrow{H_2O} LiOH + NH_3$$
$$3Mg + N_2 \longrightarrow Mg_3N_2 \xrightarrow{H_2O} Mg(OH)_2 + NH_3$$

4. Their hydroxides and carbonates are unstable and decompose on heating

$$2LiOH \xrightarrow{\Delta} Li_2O + H_2O$$
$$Mg(OH)_2 \xrightarrow{\Delta} MgO + H_2O$$
$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$
$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$$

5. Their halides and alkyls being covalent in character are soluble in organic solvents.

1.20.2 Similarities Between Lithium and Magnesium

1. Both combine directly with nitrogen and their nitrides with water give ammonia.
2. Both do not form solid bicarbonates.
3. Hydroxides of both give oxides on heating.
4. Their fluoride carbonates and phosphates are less soluble.

1.20.3 Similarities Between Beryllium and Aluminium

1. Both are silvery white, good conductors of electricity.
2. Both become passive with conc. HNO_3.
3. Their hydroxides are amphoteric.
4. They liberate hydrogen from acids and alkalis.
5. Both combine with nitrogen, carbon, silicon and boron.

Illustration 1.56

Are the oxidation state and covalency of Al in $[AlCl(H_2O)_5]^{2+}$ same?

Sol. No. The oxidation state of Al is +3 and the covalency is 6.

1.21 Periodic Trends and Chemical Reactivity

It has been observed that there is a periodic trend in certain fundamental properties such as atomic and ionic radii, ionisation enthalpy, electron gain enthalpy and valence, and the periodicity is related to electronic configuration. That is, all chemical and physical properties depend on the electronic configuration of elements.

1. **Relationships between these fundamental properties of elements with their chemical reactivity:** The atomic and ionic radii generally decrease along the period (→). As a consequence, the ionisation enthalpies generally increase (with some exceptions) and electron gain enthalpies become more negative across a period. In other words, the ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative. (It is noted that noble gases having completely filled shells have rather positive electron gain enthalpy values.) This results into high chemical reactivity at the two extremes and the lowest in the centre. Thus, the maximum chemical reactivity at the extreme left (among alkali metals) is shown by the loss of an electron leading to the formation of a cation and at the extreme right (among halogens) shown by the gain of an electron forming an anion.

   This property can be related with the reducing and oxidising behaviour of the elements.

   It can be directly related to the metallic and non-metallic character of elements. Thus, the metallic character of an element, which is highest at the extremely left decreases and the non-metallic character increases along the period.

$$\xrightarrow[\text{Non-metallic character increases}]{\text{Metallic character decreases}}$$

   The chemical reactivity of an element is shown by its reactions with oxygen and halogens. Elements on two extremes of a period easily combine with oxygen to form oxides.

   The normal oxide formed by the element on extreme left is the most basic (e.g. Na_2O), whereas that formed by the element on extreme right is the most acidic (e.g. Cl_2O_7).

   Oxides of elements in the centre are amphoteric (e.g. Al_2O_3, As_2O_3) or neutral (e.g. CO, NO, N_2O). Amphoteric oxides behave as acidic with bases and as basic with acids, whereas neutral oxides have no acidic or basic properties.

2. Among transition metals (3*d* series), the change in atomic radii is much smaller as compared to those of representative elements across the period. The change in atomic radii is still smaller among inner-transition metals (4*f*-series). The ionisation enthalpies are intermediate between those of *s*- and *p*-blocks. As a consequence, they are less electropositive than group 1 and 2 metals.

   In a group, the increase in atomic and ionic radii with the increase in atomic number generally results in a gradual decrease in ionisation enthalpies and a regular decrease (with exception in some third period elements) in electron gain enthalpies in the case of main group elements.

ILLUSTRATION 1.57

Show by a chemical reaction with water that Na_2O is a basic oxide and Cl_2O_7 is an acidic oxide.

Sol. Na_2O with water forms a strong base whereas Cl_2O_7 forms strong acid.

$$Na_2O + H_2O \longrightarrow 2NaOH$$
$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$$

Their basic or acidic nature can be qualitatively tested with litmus paper.

ILLUSTRATION 1.58

Predict the formulae of the stable binary compounds that would be formed by the following pairs of compounds:

a. Al and Cl **b.** Mg and I
c. Element 113 and F **d.** Si and S
e. Element 119 and oxygen.

Sol.

a. Al is an element of group 13 with $3e^-$ in its valence shell
Therefore, its valence = 3.
Cl is an element of group 17, with $7e^-$ in its valence shell
therefore its valence = 8 – 7 = 1.
$\therefore$ Formula = $AlCl_3$

b. Mg is an element of group 2, with $2e^-$ in its valence shell
Therefore, its valence = 2.
I is an element of group 17, with > $7e^-$ in its valence shell
Therefore, its valence = 8 – 7 = 1.
$\therefore$ Formula = $MgCl_2$

c.

Lanthanide series	Atomic number 57–71	Group 3	6th Period
Actinide series	Atomic number 89–103	Group 3	7th Period

Element (X) (At. no. = 113) lies in group 13, and 7th period. Hence, its outer shell electronic configuration is $7s^2 7p^1$ therefore its valence = 3.
F belongs to group 17 with $7e^-$ in its valence shell. Therefore its valence = 8 – 7 = 1.
$\therefore$ Formula = XF_3.

d. Si is an element of group 14 with $4e^-$ in its valence shell
Therefore, its valence = 4.
S is an element of group 16 with $6e^-$ in its valence shell
Therefore, its valence = 8 – 6 = 2.
Formula = SiS_2

e. Element (X) (Z = 119) lies in group 1, and 8th period. Hence its outer shell electronic configuration is $8s^1$. Therefore, its valence = 1
O is an element of group 16 with $6e^-$ in its valence shell.
Therefore, its valence = 8 – 6 = 2.
Formula = X_2O

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Atomic number				104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
	119	120																

$\longleftarrow$ *s*-block $\longrightarrow$ $\longleftarrow$ *d*-block $\longrightarrow$ $\longleftarrow$ *p*-block $\longrightarrow$

1.22 MAGNETIC PROPERTIES OF ELEMENTS

Each element has some kind of magnetic properties associated with it. These properties are direct consequence of the electronic configuration of the atom. When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: **(i)** Diamagnetism and **(ii)** Paramagnetism.

1. Diamagnetic substances are weakly repelled by the magnetic applied field and have all the electrons paired in their atoms, e.g. NaCl and H_2O.
2. Paramagnetic substances are attracted by the magnetic applied field and has one or more unpaired electrons in their atoms, e.g. Cu^{2+}, Fe^{3+}, Cr^{3+} and O_2.

   Substances which are strongly attracted by the magnetic applied field are said to be **ferromagnetic**. In fact, ferromagnetism is an extreme form of paramagnetism.
3. Ferromagnetic substances keep their magnetism even after the field is remained while paramagnetic and diamagnetic substances fail to do so. Fe, Co and Ni are some examples of ferromagnetic substances.
4. Paramagnetism is due to the presence of unpaired electrons. An electron in an atom which has two types of motion, one of its motion is about the nucleus (orbital angular momentum), and the other is its spin about its own axis (spin angular momentum).

   A single electron spinning about its own axis generates a magnetic field. For two electrons in an orbital, the spins are opposite and hence the fields cancel each other, hence they have zero magnetic moment value.
5. When there are one or more unpaired electrons in them, the unpaired electron gives rise to a magnetic field on account of its spin and because of the angular orbital moment.

6. Magnetic moment (μ_{S+L}) of the first row of transition metal ions is given by general formula:

$$\mu_{S+L} = \sqrt{4S(S+1)+L(L+1)}$$

where, S is the sum of spin quantum numbers and L = sum of the orbital angular momentum quantum numbers.

For an electron, spin quantum number, $S = \pm 1/2$. Hence, $S = s \times n$ (n = number of unpaired electrons).

For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these the magnetic moment is determined by the number of unpaired electrons and is calculated by using 'spin only' formula. Taking $L = 0$, the magnetic moment is given as

$$\mu_s = \sqrt{4S(S+1)}$$

In terms of n (number of unpaired electrons), μ_s is given by

$$\mu_s = \sqrt{n(n+2)} \text{ BM (Bohr magneton)}$$

7. It is measured in Bohr magneton (BM).

$$1 \text{ BM} = \frac{eh}{4\pi mc} = 9.27 \times 10^{-21} \text{ ergs gauss}^{-1}$$

or $9.27 \times 10^{-24} \times$ J Tesla^{-1} or 9.27×10^{-24} A m^2

where h is the Planck's constant, e is the electronic charge, c is the velocity of light and m is the mass of electrons.

Note: The orbital motion in $4f$ orbitals is not quenched, as in the case of d-block elements. Hence the observed paramagnetism in $4f$-block elements is due to both orbital motion of the electron and its spinning round its axis.

When $n = 1, \mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ BM

$n = 2, \mu_s = \sqrt{2(2+2)} = \sqrt{8} = 2.83$ BM

$n = 3, \mu_s = \sqrt{3(3+2)} = \sqrt{15} = 3.87$ BM

and so on.

$\therefore \mu_s \propto n$ (number of unpaired e^-'s).

ILLUSTRATION 1.59

Give the decreasing order of magnetic moment of the following:

a. Ca **b.** Al **c.** N **d.** O

Sol.

a. Electronic configuration of Ca = $4s^2$; $n = 0$, $\mu = 0$.

b. Electronic configuration of Al = $3s^2\,3p^1$; $n = 1$, $\mu = \sqrt{3}$.

c. Electronic configuration of N = $2s^2\,2p^3$; $n = 3$, $\mu = \sqrt{15}$.

d. Electronic configuration of O = $2s^2\,2p^4$; $n = 2$, $\mu = \sqrt{8}$

$\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

$2p$

Hence, the decreasing order of magnetic moment or paramagnetism is

$$N > O > Al > Ca$$

ILLUSTRATION 1.60

Which element in $3d$, $4d$ and $5d$ transition series has the highest paramagnetism in

a. elemental form **b.** + 1 O.S.

c. + 2 O.S. **d.** + 3 O.S.

[O.S. = oxidation state]

Sol.

a. In elemental form:

3d series: Cr ($Z = 24$) $\Rightarrow 3d^5\,4s^1$; $n = 6$, $\mu = \sqrt{6+(6+2)} = \sqrt{48}$ BM

4d series: Mo ($Z = 42$) $\Rightarrow 4d^5\,5s^1$; $n = 6$, $\mu = \sqrt{48}$ BM

5d series: W ($Z = 74$) $\Rightarrow 5d^4\,6s^2$; $n = 4$, $\mu = \sqrt{24}$ BM

But Re has the highest number of unpaired e^-, as shown:

Re ($Z = 75$) $\Rightarrow 5d^5\,6s^2$; $n = 5$, $\sqrt{35}$ BM

b. In +1 oxidation state:

3d series: Mn ($Z = 25$) $\Rightarrow 3d^5\,4s^2$, $Mn^{1+} = 3d^5\,4s^1$; $n = 6$, $\mu = \sqrt{48}$ BM

4d series: Tc ($Z = 43$) $\Rightarrow 4d^5\,5s^2$, $Tc^{1+} = 4d^5\,5s^1$; $n = 6$, $\mu = \sqrt{48}$ BM

5d series: Re ($Z = 75$) $\Rightarrow 5d^5\,6s^2$, $Re^{1+} = 5d^5\,6s^1$; $n = 6$, $\mu = \sqrt{48}$ BM

c. In +2 oxidation state:

3d series: Mn ($Z = 25$) $\Rightarrow 3d^5\,4s^2$, $Mn^{2+} = 3d^5, 4s^0$; $n = 5$, $\mu = \sqrt{35}$ BM

4d series: Tc ($Z = 43$) $\Rightarrow 4d^5\,5s^2$, $Tc^{2+} = 4d^5\,5s^0$; $n = 5$, $\mu = \sqrt{35}$ BM

5d series: Re ($Z = 75$) $\Rightarrow 5d^5\,6s^2$, $Re^{2+} = 5d^5\,6s^0$; $n = 5$, $\mu = \sqrt{35}$ BM

d. In +3 oxidation state:

3d sereis : Fe ($Z = 26$) $\Rightarrow 3d^6\,4s^2$; $Fe^{3+} = 3d^5\,4s^0$; $n = 5$, $\mu = \sqrt{35}$ BM

4d series : Ru ($Z = 44$) $\Rightarrow 4d^7\,5s^1$ (exception electronic configuration).

$\therefore Ru^{3+} = 4d^5\,5s^0$; $n = 5$, $\mu = \sqrt{35}$ BM

5d series: Os ($Z = 76$) $\Rightarrow 5d^6\,7s^2$; $Os^{3+} = 5d^5\,7s^0$; $n = 5$, $\mu = \sqrt{35}$ BM

Note:

i. From the above calculation it is clear that in the elemental form (zero OS), group 6 has the highest μ, except W, in $5d$ series, but it is Re of group 7.

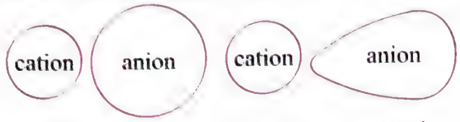
ii. In +1 OS, group 7 has the highest μ.

iii. In +2 OS, again group 7 has the highest μ.

iv. In +3 OS, group 8 has the highest μ.

1.23 FAJANS' RULE AND CHANGE OF IONIC CHARACTER TO COVALENT CHARACTER

When two oppositely charged ions of unequal size approach each other closely (during formation of an electrovalent bond), the ion smaller in size attracts the outermost electrons of the other ion and repels its nuclear charge. The net result is distortion or polarisation of the bigger ion. This distortion is usually done by the cation as its size is smaller than the anion (Fig. 1.14).



(a) No polarisation **(b)** Polarised anion

Fig. 1.14 Representation of polarisation

The electron cloud of anion no longer remains symmetrical but is elongated towards the cations. The ability of a cation to polarise the nearby anion is called its **polarising power** and the tendency of an anion to get distorted or deformed or polarised by the cation is called its **polarisability**. Due to polarisation, sharing of electrons occurs between two ions to some extent and the bond shows some covalent character. This is shown in Fig. 1.14.

Polarising power of cation (ϕ) is calculated as

$$\phi = \frac{\text{Ionic charge}}{(\text{Ionic radius})^2}$$

The magnitude of polarisation depends upon a number of factors or the increased covalent character is favoured by a number of factors. These factors were suggested by Fajans' and are known as **Fajans' rules**.

1.23.1 FAJANS' RULES

1. **Charge on the cation:** As the charge on the cation increases, its tendency to polarise the anion increases. This brings more and more covalent nature in the electrovalent compound. For example, in the case of NaCl, $MgCl_2$ and $AlCl_3$ charge of cation increases and polarisation increases, thereby covalent character becomes more and more as the charge on the cation increases.

Cation	Cation charge	Formula of the chloride	Melting point of the chloride, °C	
$Na^{⊕}$	+1	NaCl	800	Covalent
Mg^{2+}	+2	$MgCl_2$	712	Character
Al^{+3}	+3	$AlCl_3$	Sublimes	Increases ↓

Similarly, lead forms two chlorides $PbCl_2$ and $PbCl_4$ having charges +2 and +4 respectively. $PbCl_4$ shows covalent nature.

In general, if a metal forms more than one halide, the halide having higher charge on the cation (i.e. higher oxidation state) is usually more covalent in nature in comparison to halide having a cation with lower charge, i.e. lower oxidation state or in other words, the melting point of the halide having higher oxidation state is less than the melting point of halide having lower oxidation state.

2. **Size of the cation:** Polarisation of the anion increases as the size of the cation decreases, i.e. the electrovalent compounds having smaller cations show more of the covalent nature. For example, in the case of halides of alkaline earth metals the covalent character decreases.

Cation	Radius of the cation (Å)	Formula of the chloride	Melting point of the chloride, °C		
Be^{2+}	0.31	$BeCl_2$	405	↑ Covalent character increases	↑ Melting point decreases
Mg^{2+}	0.65	$MgCl_2$	712		
Ca^{2+}	0.99	$CaCl_2$	772		
Sr^{2+}	1.13	$SrCl_2$	872		
Ba^{2+}	1.35	$BaCl_2$	960		

Low melting point indicates more covalent nature.

3. **Size of the anion:** The larger the size of the anion, more easily it will be polarised by the cation, i.e. as the size of the anion increases for a given cation, the covalent character increases. For example, in the case of halides of calcium, the covalent character increases from $F^{\ominus}$ anion to $I^{\ominus}$ anion.

Cation	Anion	Anion size (Å)	Formula of the halide	Melting point of the halide, °C		
Ca^{2+}	$F^{\ominus}$	1.36	CaF_2	1932	Covalent character increases ↓	Melting point decreases ↓
	$Cl^{\ominus}$	1.81	$CaCl_2$	772		
	$Br^{\ominus}$	1.95	$CaBr_2$	730		
	$I^{\ominus}$	2.16	CaI_2	575		

Similarly, in the case of trihalides of aluminium, the covalent character increases with the increase in size of the halide anion.

$$\xrightarrow[\text{Covalent character increases as the size of the halide ion increases}]{AlF_3 < AlCl_3 < AlBr_3 < AlI_3}$$

4. **Configuration of the cation:** The cations with 18 electrons in the outermost shell bring greater polarisation of the anion than those with inert gas configuration, even if both the cations have same size and same charge. For example, CuCl is more covalent than NaCl.

Ion	$Cu^{⊕}$	$Na^{⊕}$
Size	0.96 Å	0.95 Å
Compound	CuCl	NaCl
Melting point	442°C	800°C

In general, all those electrovalent compounds having high values of polarisation (more covalent character) are found to be less soluble in water but more soluble in organic solvents. The following examples support this view:

a. Sulphides are less soluble in water than oxides of the same metal.

b. Lithium salts are soluble in organic solvents.

c. Beryllium compounds are less soluble than the corresponding other alkaline earth metal compounds.

d. The solubility of aluminium halides decreases from AlF_3 to AlI_3.

Points to remember:

1. On moving down a group, the polarising power of the cations goes on decreasing,
2. Polarising power of the cations increases in moving from the left to the right in a period.
3. The polarisability of the anions by a given cation decreases in moving from the left to the right in a period.
4. The polarisability of the anions by a given cation increases moving down a group.
5. Increase of polarisation brings more of covalent character in a compound. The increased covalent character is indicated by the decrease in melting point of the compound.

Examples:

Polarisation increases →

Covalent character increases →

Melting point decreases →

a.	m.pt. (°C)	NaF < NaCl < NaBr < NaI (Size of anion increases) 988 > 801 > 755 > 651
b.	m.pt. (°C)	CaF_2 < $CaCl_2$ < $CaBr_2$ < CaI_2 (Size of anion increases) 1392 > 772 > 730 > 575
c.	m.pt. (°C)	$BaCl_2 < SrCl_2 < CaCl_2 < MgCl_2 < BeCl_2$ (Size of cation decreases) 960 > 872 > 772 > 712 > 405
d.	m.pt. (°C)	NaCl < $MgCl_2$ < $AlCl_3$ (Charge on the cation increases) 801 > 712 > sublimes
e.	m.pt. (°C)	LiCl < $BeCl_2$ < BCl_3 < CCl_4 (Size of the cation decreases)
f.	$GeCl_2 < GeCl_4$; $SnCl_2 < SnCl_4$; $PbCl_2 < PbCl_4$	
g.	$HF < H_2O < NH_3 < CH_4$	
h.	HF < HCl < HBr < HI	
i.	NaCl < CuCl; NaI < AgI	

1.23.2 Comparison in the Properties of Covalent and Ionic Compounds

Covalent character increases	Ionic character increases
1. Melting point decreases	1. Melting point increases
2. Solubility in polar solvent decreases	2. Solubility in polar solvent increases
3. Solubility in non-polar solvent increases	3. Solubility in non-polar solvent decreases
4. Acidic property of oxides increases	4. Basic property of oxides increases
5. Non-metallic character increases	5. Metallic character increases

ILLUSTRATION 1.61

Give the decreasing order of the acidic properties of oxides.

a. ZnO b. KO_2 c. P_2O_5 d. MgO

Sol. Since the anions are same, so first check the charges on the cations.

The higher the charge on the ions, the more covalent or more acidic is the nature.

a. $Zn^{2+}\,O^{2-}$ b. $K^{\oplus}\,O_2^{\ominus}$

c. $\overset{+5\times 2}{P_2}\;\overset{-2\times 5}{O_5}$ d. $Mg^{2+}O^{2-}$

Since the charge on MgO and ZnO is same but the size of Zn^{2+} < the size of Mg^{2+} (small cation).

OR

Zn^{2+} has *d*-orbitals, so more covalent.

So. decreasing order of acidic character is :

$P_2O_5 > ZnO > MgO > KO_2$ (III > I > IV > II)

ILLUSTRATION 1.62

Give the decreasing order of the basic properties of oxides.

a. Tl_2O b. Al_2O_3 c. Tl_2O_3 d. Ga_2O_3

Sol. Anions are same, so check the charges on the cation. The lesser the charge on the ions, the more ionic or more basic in the nature.

a. $\overset{+1\times 2}{Tl_2}\;\overset{-2}{O}$ b. $\overset{+3\times 2}{Al_2}\;\overset{-2\times 3}{O_3}$ c. $\overset{+3\times 2}{Tl_2}\;\overset{-2\times 3}{O_3}$ d. $\overset{+3\times 2}{Ga_2}\;\overset{-2\times 3}{O_3}$

Charges on the cations in b., c., and d. are same so check the sizes of the cations. Large cation, more ionic and more basic. All of them belong to group 13. Therefore, size of $Tl^{3+} > Ga^{3+} > Al^{3+}$.

Hence decreasing basic oxides :

$Tl_2O > Tl_2O_3 > Ga_2O_3 > Al_2O_3$ (a > c > d > b)

ILLUSTRATION 1.63

Give the decreasing order of melting points of the following compounds:

a.	I. NaF	II. NaCl	III. NaBr	IV. NaI
b.	I. CaI_2	II. $CaBr_2$	III. $CaCl_2$	IV. CaF_2
c.	I. $BaCl_2$ V. $BeCl_2$	II. $SrCl_2$	III. $CaCl_2$	IV. $MgCl_2$
d.	I. NaCl	II. $MgCl_2$	III. $AlCl_3$	
e.	I. CCl_4	II. BCl_3	III. $BeCl_2$	IV. LiCl

Sol.

a. NaF > NaCl > Na Br > NaI

m.pt. (°C) 988 > 801 > 755 > 651

∴ I > II > III > IV

[Size of anion increases, covalent character increases and m.pt. decreases]

b. $CaF_2 > CaCl_2 > CaBr_2 > CaI_2$ (IV > III > II > I)

m.pt. (0°C) 1392 > 772 > 730 > 575

Since cation is same the charges on the ions are also same. So, the size of anion increases (group 17 ions), covalent character increases and m.pt. decreases.

c. $BaCl_2 > SrCl_2 > CaCl_2 > MgCl_2 > BeCl_2$ (I > II > III > IV > V)

m.pt. (°C) 960 > 872 > 772 > 712 > 405

Since anion is same the charges on the ions are also same. So, the size of cation decreases (group 2 ions), covalent character of cation decreases and m.pt. increases.

d. $\overset{+1}{Na}Cl > \overset{+2}{Mg}Cl_2 > \overset{+3}{Al}Cl_3$ (I < II < III)

The charge on the cation increases, covalent character increases and m.pt. decreases.

e. $\overset{+1}{Li}Cl > \overset{+2}{Be}Cl_2 > \overset{+3}{B}Cl_3 > \overset{+4}{C}Cl_4$ (IV > III > II > I)

The charge on the cation increases, covalent character increases and m.pt. decreases.

ILLUSTRATION 1.64

Give the decreasing order of covalent character of the following compounds.

a.	I. $GeCl_2$	II. $GeCl_4$	III. $SnCl_2$	IV. $SnCl_4$
	V. $PbCl_2$	VI. $PbCl_4$		
b.	I. CH_4	II. NH_3	III. H_2O	IV. HF
c.	I. HF	II. HCl	III. HBr	IV. HI
d.	I. AgI	II. NaI	III. CuI	IV. NaCl

Sol.

a. First check the charge, higher the charge on the ions, more is the covalent character (since anion is same)

I. $\overset{+2}{Ge}Cl_2$ **II.** $\overset{+4}{Ge}Cl_4$ **III.** $\overset{+2}{Sn}Cl_2$

IV. $\overset{+4}{Sn}Cl_4$ **V.** $\overset{+2}{Pb}Cl_2$ **VI.** $\overset{+4}{Pb}Cl_4$

So, group compounds of higher charges appear first and then come the lower charges. All the compounds belong to group 14. Now check the sizes of the cation, the small cation shows more covalent character.

Hence the decreasing order of covalent character is

$$\left(\underset{\text{Size increases and +4 charge}}{\xrightarrow{\overset{4+}{Ge}Cl_4 > \overset{4+}{Sn}Cl_4 > \overset{4+}{Pb}Cl_4}}\right) > \left(\underset{\text{Size increases and +2 charge}}{\xrightarrow{\overset{2+}{Ge}Cl_2 > \overset{2+}{Sn}Cl_2 > \overset{2+}{Pb}Cl_2}}\right)$$

i.e. (II > IV > VI > I > III > V)

b. Check the charges on the ions. Higher the charge on the ions, more is the covalent character.

So, the decreasing order of covalent character is

$$\underset{\text{decreasing charges on the ions}}{\xrightarrow{\overset{+4\,-4}{CH_4} > \overset{+3\,-2}{NH_3} > \overset{+1\,\times 2\,-2}{H_2O} > \overset{\oplus}{HF}}} \text{ (I > II > III > IV)}$$

c. Since charges on the ions (cation and anion) are same and cation ($H^{\oplus}$ ion) is also same. So, check the size of anion. Large anion, more is the covalent character (all anions of group 17).

So, the decreasing order of covalent character is

HI > HBr > HCl > HF (IV > III > II > I)

d. Charges on the ions are same.

Size of $Cu^{\oplus} \approx$ Size of $Na^{\oplus}$

Moreover, $Ag^{\oplus}$ and $Cu^{\oplus}$ have *d* configuration.

Size of $Ag^{\oplus}$ > Size of $Cu^{\oplus}$

Small cation, with *d* configuration is more covalent. Large anion with *d* configuration is more covalent.

So, the decreasing order of covalent character is

CuI > AgI > NaI > NaCl (III > I > II > IV)

ILLUSTRATION 1.65

Give the decreasing pH of aqueous solution of the following compounds:

a. NaCl **b.** $MgCl_2$ **c.** $AlCl_3$ **d.** PCl_5

Sol. Since anions are same, so higher the charge on the ions, more covalent and more acidic and hence less pH.

So, the decreasing order of pH is

$$\underset{\substack{\text{Increasing order of acidic or}\\ \text{decreasing order of basic character}}}{\xrightarrow{\overset{1+}{Na}Cl > \overset{2+}{Mg}Cl_2 > \overset{3+}{Al}Cl_3 > \overset{5+}{P}Cl_5}} \text{ [a. > b. > c. > d.]}$$

1.24 INERT PAIR EFFECT

In groups 13–16 as we move down the group the stability of lower oxidation state increases. For example in group 13, Tl is more stable in +1 OS than +3. Similarly in groups 14 and 15, Pb and Bi are more stable in +2 and +3 OS than +4 and +5 OS. This is because as we move down the group, the tendency of *s*-electron of the valence shell to participate in bond formation decreases. This reluctance of the *s*-electron to unpair and participate in bond formation is called inert pair effect. This is due to poor or ineffective shielding of ns^2 electrons of valence shell by intervening *d* and *f* electrons.

The inert pair effect becomes more predominant as we move down the group because of the increased nuclear charge which outweighs the effect of the corresponding increase in atomic size and therefore ns^2 electrons become more reluctant to participate in bond formation.

Note: OS in circle is more predominant in bond formation.

Electronic configuration	Group 13	OS
[He] $2s^2 2p^1$	B	+3
[Ne] $3s^2 3p^1$	Al	+3
[Ar] $3d^{10} 4s^2 4p^1$	Ga	+1 +3
[Kr] $4d^{10} 5s^2 5p^1$	In	+1 +3
[Xe] $4f^{14} 5d^{10} 6s^2 6p^1$	Tl	+1
	Group 14	**OS**
[He] $2s^2 2p^2$	C	+4
[Ne] $3s^2 3p^2$	Si	+4
[Ar] $3d^{10} 4s^2 4p^2$	Ge	+4 +2
[Kr] $4d^{10} 5s^2 5p^2$	Sn	+2 +4
[Xe] $4f^{14} 5d^{10} 6s^2 6p^2$	Pb	+2

	Group 15	OS
[He] $2s^2 2p^3$	N	+3
[Ne] $3s^2 3p^3$	P	+5
[Ar] $3d^{10} 4s^2 4p^3$	As	+3 +5
[Kr] $4d^{10} 5s^2 5p^3$	Sb	+3 +5
[Xe] $4f^{14} 5d^{10} 6s^2 6p^3$	Bi	+3

1.25 FACTORS THAT DETERMINE THE FORMATION (OR STABILITY) OF COMPOUNDS

It may be noted that some compounds are stable while others are not. In other words, some compounds are formed easily some or not, e.g.

1. NH_3 exists, but NH_5 does not exist.
2. NCl_3 exists, but NCl_5 does not exist.
3. PCl_5 exists, but PBr_5 or PI_5 does not exist.
4. PH_3 exists, but PH_5 does not exist.
5. TlCl, $PbCl_2$ and $BiCl_3$ are more stable than $TlCl_3$, $PbCl_4$ and $BiCl_5$.
6. IF_7 exists, but ICl_7 does not exist.
7. $AlCl_3$ exists as bridged dimer, but BCl_3 does not exist.

Formation or stability of compounds can be explained by the following factors:

a. High EN of the element to excite electrons from central atom to vacant orbitals
b. Presence of vacant orbitals
c. Inert pair effect
d. Sizes of the cation and anion

Explanation:

1. NH_3 exists, but NH_5 does not exist.

Valence electronic configuration of N:

$2s^2$ $2p^3$

$\boxed{\uparrow\downarrow}$ $\boxed{1}\boxed{1}\boxed{1}$

N atom does not have vacant d orbitals. Moreover, the EN of H atom is not sufficient to excite the $2s$ electrons to vacant orbitals. So, NH_5 does not exist.

However, NH_3 exists since N atom can form 3 covalent bonds with 3H atoms by sharing 3 electrons from 3H atom to complete its octate.

2. NCl_3 exists, but NCl_5 does not exist.

Although EN of Cl atom is very high, it can excite $2s$ electrons to vacant orbitals. But N atom does not have vacant d orbitals so NCl_5 does not exist.

3. PCl_5 exists, but PBr_5 and PI_5 do not exist. Valence electronic configuration of P $\Rightarrow 3s^2\ 3p^3$

$3s^2$ $3p^3$ $3d^0$

$\boxed{\uparrow\downarrow}$ $\boxed{1}\boxed{1}\boxed{1}$ $\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }$

Vacant d orbitals

Although P atom has vacant $3d$ orbitals and EN of Cl is sufficiently high to excite $3s$ electrons to $3d$ orbitals as

$3s^1$ $3p^3$ $3d^1$

$\boxed{1}$ $\boxed{1}\boxed{1}\boxed{1}$ $\boxed{1}\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }$

So, PCl_5 can form five covalent bonds with 5 Cl atoms by formation of sp^3d hybridisation.

But EN of Br and I atoms are not so high to excite $3s$ electrons to $3d$ orbitals, so PBr_5 and PI_5 do not exist.

4. PH_3 exists but PH_5 does not exist.

Although P atom has vacant $3d$ orbitals but EN of H atom is not sufficient to excite $3s$ electrons to $3d$ orbitals. So, PH_5 does not exist.

5. TlCl, $PbCl_2$ and $BiCl_3$ exist, but $TlCl_3$, $PbCl_4$ and $BiCl_5$ do not exist.

Valence electronic configuration of Tl $= 6s^2\ 6p^1 \Rightarrow$

$6s^2$ $6p^1$

$\boxed{\uparrow\downarrow}$ $\boxed{1}\boxed{\ }\boxed{\ }$

vacant p-orbital

Valence electronic configuration of Pb $\Rightarrow 6s^2\ 6p^2 \Rightarrow$

$6s^2$ $6p^2$

$\boxed{\uparrow\downarrow}$ $\boxed{1}\boxed{1}\boxed{\ }$

vacant p-orbital

Valence electronic configuration of Bi $\Rightarrow 6s^2\ 6p^3\ 6d^0$

$6s^2$ $6p^3$ $6d^0$

$\Rightarrow \boxed{\uparrow\downarrow}$ $\boxed{1}\boxed{1}\boxed{1}$ $\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }$

vacant d-orbital

Although both factors, i.e. (i) high EN of Cl atom to excite $6s$ electrons to $6p$ orbitals in Tl and Pb and to $6d$ orbitals in Bi and (ii) vacant orbitals to accommodate the excited $6s$ electrons, are present in all the compounds, yet $TlCl_3$, $PbCl_4$ and $BiCl_5$ are not stable compounds.

This is due to the **inert pair effect** (refer to Section 1.24).

6. IF_7 exists, but ICl_7 does not exist.

Valence electronic configuration of I $= 5s^2\ 5p^5\ 5d^0$

$5s^2$ $5p^5$ $5d^0$

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{1}$ $\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }$

Vacant d orbital.

Both factors, i.e. (i) high EN of F and Cl atoms and (ii) vacant $5d$ orbitals are present.

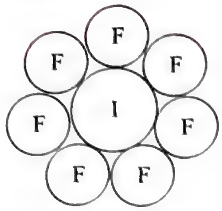
High EN of F and Cl can excite $5s$ and $5p$ electrons to $5d$ orbitals as

$5s^1$ $5p^3$ $5d^3$

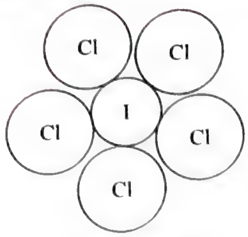
$\boxed{1}$ $\boxed{1}\boxed{1}\boxed{1}$ $\boxed{1}\boxed{1}\boxed{1}\boxed{\ }\boxed{\ }$

So, both IF_7 and ICl_7 can form 7 covalent bonds with 7F or 7 Cl atoms by formation of sp^3d^3 hybridisation. But ICl_7 does not exist due to the following reason:

Size of $F^{(-)}$ ion is very small and I can accommodate 7 $F^{(-)}$ ions around it, but it cannot accommodate 7 large size $Cl^{(-)}$ ions around it, as shown.



IF_7 molecule

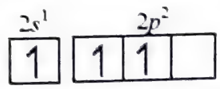


ICl_5 molecule

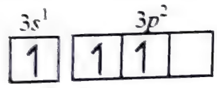
7. $AlCl_3$ exists as bridged dimer (e.g. Al_2Cl_6), but BCl_3 does not exist.

Valence electronic configuration of B in the ground state $= 2s^2\ 2p^1$

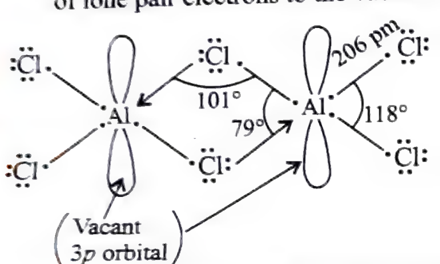
Valence electronic configuration of B in the excited state

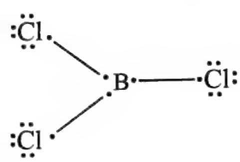


Valence electronic configuration of Al in the excited state



Bridged dimer structure of $AlCl_3$ is formed by the donation of lone pair electrons to the vacant $3p$ orbitals as shown:





Structure of BCl_3

(Structure of bridged dimer of $AlCl_3$)

Although B atom also has vacant $2p$ orbitals, it should also form bridged dimeric structure of BCl_3.

But boron halides exist as monomer because boron (B) atom is so small that it cannot accommodate four large sized halide ions around it with 2 coordinate and 2 covalent bonds.

1.26 IONIC BOND

Kossel and Lewis explained that the formation of ionic bond primarily depends upon (i) The ease of formation of positive and negative ions from the respective neutral atoms, and (ii) The lattice of the compound, i.e. the arrangement of positive and negative ions in the solid, e.g.

$$M_{(g)} \longrightarrow M^{\oplus}_{(g)} + e^- \text{ (IE)}$$

$$X_{(g)} + e^- \longrightarrow X^{\ominus}_{(g)} \ (\Delta_{eg}H^{\ominus})$$

It is evident that the ionic bond will be formed more easily between elements with comparatively low IE and elements with comparatively low (negative) $\Delta_{eg}H^{\ominus}$.

Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements.

The $\overset{\oplus}{NH_4}$ ion is made up of two non-metallic elements which is an exception.

Ionic compounds in the crystalline state consist of orderly three-dimensional arrangement of cations and anions held together by coulombic interaction energies. These ionic compounds crystallise in different crystal structures. This is due to the difference in the size of the ions, their packing arrangements and other factors.

In ionic compounds, the sum of IE and $\Delta_{eg}H^{\ominus}$ may be positive but the crystal structure gets stabilised due to the energy released in the formation of the crystal lattice.

Example:

$$Na_{(g)} \longrightarrow Na^{\oplus}_{(g)} + e^- \qquad (\text{IE} = 495.8 \text{ kJ mol}^{-1})$$

$$Cl_{(g)} + e^- \longrightarrow Cl^{\ominus}_{(g)} \qquad (\Delta_{eg}H^{\ominus} = -348.7 \text{ kJ mol}^{-1})$$

$$Na_{(g)} + Cl_{(g)} \rightarrow Na^{\oplus}_{(g)} + Cl^{\ominus}_{(g)} \qquad \Delta H^{\ominus} = 147.1 \text{ kJ mol}^{-1}$$

The sum of the above two (i.e. 147.1 kJ mol^{-1}) is more than compensated for by the enthalpy of lattice formation of NaCl which is equal to 788 kJ mol^{-1}.

Thus, a qualitative measure of the stability of an ionic compound is provided by the enthalpy of lattice formation.

1.26.1 LATTICE ENTHALPY

Lattice enthalpy ($\Delta_U H^{\ominus}$) is the amount of energy released when crystal lattice of one mole of solid ionic compound is formed from their gaseous constituent ions. For example,

$$Na^{\oplus}_{(g)} + Cl^{\ominus}_{(g)} \rightarrow NaCl_{(s)} \ \Delta_U H^{\ominus} = -788 \text{ kJ mol}^{-1}$$

OR

Lattice enthalpy ($\Delta_U H^{\ominus}$) is the amount of energy required to completely separate one mole of solid ionic compound into its gaseous constituent ions. For example,

$$NaCl_{(s)} \rightarrow Na^{\oplus}_{(g)} + Cl^{\ominus}_{(g)};\ \Delta_U H^{\ominus} = 788 \text{ kJ mol}^{-1}$$

This process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charges.

Since the solid crystal is three dimensional, therefore, lattice enthalpy cannot be calculated directly from the interaction of forces of attraction and repulsion only. Hence, factors associated with the crystal geometry have to be included.

Lattice enthalpy depends on the following factors:

1. It depends on the size of the ions. If the sizes of cations and anions are comparable, then a strong lattice is formed and more (negative) energy is released.
2. It depends on the magnitude of charges on the ions. If the charges on the ions are greater, than a strong lattice is formed and more (negative) energy is released.
3. It increases from uni-univalent ionic solid (e.g. NaCl) to uni-bivalent (e.g. $MgCl_2$) and then to bi-bivalent ionic solid (e.g. MgO).
4. The larger the magnitude of lattice energy, the greater will be the stability of ionic solid.
5. Ionic solids having higer value of lattice energies have higher melting, boiling points and are very hard.
6. Ionic solids with high value of lattice energies have low solubility in water (polar solvents).

7. Generally the lattice energy decreases down the group and increases along the period.

The first theoretical interpretation of lattice energy was given by Born and Lande as

$$U_0 \propto \frac{|Z^{\oplus}||Z^{\ominus}|}{r_0}$$

Where U_0 is the lattice energy.

[The above equation helps to interact with all the other ions besides the nearest neighbours]

$|Z^{\oplus}|$ = Charge on the positive ion (only magnitude value)

$|Z^{\ominus}|$ = Charge on the negative ion (only magnitude value)

r_0 = Inter-ionic distances

8. It is evident that the lattice energy becomes stronger (i.e. more negative value) as r_0, the inter-ionic distance decreases, i.e.

$$U_0 \propto \frac{1}{r_0}$$

Example:

	r_0 (Å)	U_0 (kJ mol^{-1})
LiF	2.01	– 1004
CsI	3.95	–527

9. The lattice energy depends on the product of the ionic charges, i.e.

$$U_0 \propto |Z^{\oplus}|\,|Z^{\ominus}|$$

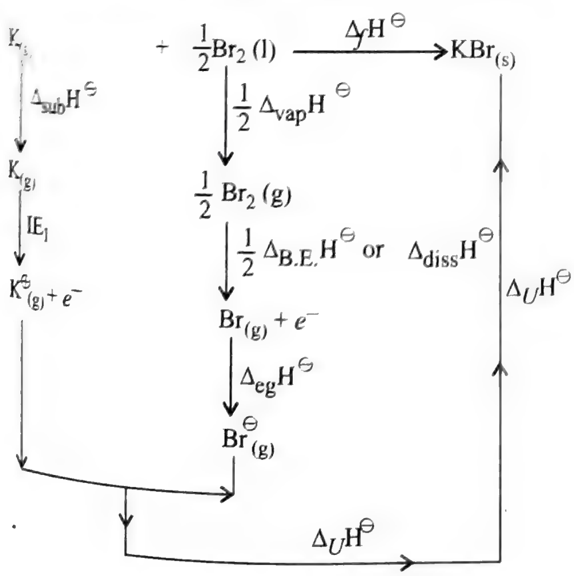
Example:

	r_0(Å)	$\lvert Z^{\oplus}\rvert\,\lvert Z^{\ominus}\rvert$	U_0 (kJ mol^{-1})
LiF	2.01	1 × 1	– 1004
MgO	2.10	2 × 2	– 3933

1.26.2 Determination of Lattice Energy

It is determined by the use of Born–Haber cycle, which is based on the Hess's law of heat summation.

For example, lattice energy of KBr(s) is determined as:



$$\therefore \ \Delta_f H^{\ominus} = \Delta_{sub}H^{\ominus} + IE_1 + \frac{1}{2}\Delta_{vap}H^{\ominus} + \frac{1}{2}\Delta_{B.E}H^{\ominus} + \Delta_{eg}H^{\ominus} + \Delta_U H^{\ominus}$$

$$\therefore \ \Delta_U H^{\ominus} = \Delta_f H^{\ominus} - \Delta_{sub}H^{\ominus} - IE_1 - \frac{1}{2}\Delta_{vap}H^{\ominus} - \frac{1}{2}\Delta_{B.E}H^{\ominus} - \Delta_{eg}H^{\ominus}.$$

Note: EN and hydration $\Delta H^{\ominus}$ can not be determined by Born Haber cycle since these two factors are not involved in the above cycle.

1.26.3 Applications of Lattice Energy

Formation of oxides, peroxides and superoxides of group 1 and group 2 elements: When heated with excess of O_2, Li forms monoxides (Li_2O), Na forms peroxides (Na_2O_2) and K, Rb and Cs. form superoxides having general formula (MO_2).

Similarly, when heated with oxygen, Be, Mg and Ca form monoxide (MO) while Sr and Ba form peroxide (MO_2).

Explanation: This is due to the comparable sizes of cation and anion, which forms the strongest lattice with the release of high energy.

Example:

1. $4Li + O_2 \xrightarrow{\Delta} 2Li_2O$ [size of 2 $Li^{\oplus}$ ion is comparable with the size of O^{2-} (oxide) ion].
2. $2Na + O_2 \xrightarrow{\Delta} Na_2O_2$ [size of 2 $Na^{\oplus}$ ion is comparable with the size of O_2^{2-} (peroxide) ion].
3. $K + O_2 \xrightarrow{\Delta} KO_2$ [size of $K^{\oplus}$ ion is comparable with the size of $O_2^{\ominus}$ (superoxide) ion].
4. Similarly, sizes of Be^{2+}, Mg^{2+} and Ca^{2+} ions are comparable with O^{2-} (oxide) ion in MO, where M = Be, Mg and Ca.
5. Sizes of Sr^{2+} and Ba^{2+} ions are comparable with O_2^{2-} (peroxide) ion in MO_2, where M = Sr and Ba.

Alternative explanation: Due to high charge density $\left(\frac{\text{charge}}{\text{size}}\ \text{ratio}\right)$ of $Li^{\oplus}$, it attracts the negative charge so strongly that it does not allow the oxide anion (O^{2-}) to combine with another oxygen atom to form peroxide ion, O_2^{2-}.

Whereas $Na^{\oplus}$ ion has comparatively less charge density than $Li^{\oplus}$ ion, so it cannot prevent O^{2-} ion to combine with another oxygen atom to form peroxide ion.

$$\left[\underset{\text{oxide}}{O^{2-}} + \frac{1}{2}O_2 \rightarrow O_2^{2-}\ \text{(peroxide)}\right]$$

On the other hand, larger $K^{\oplus}$, $Rb^{\oplus}$ and $Cs^{\oplus}$ ions have still lesser charge density which cannot prevent even peroxide ion (O_2^{2-}) to combine with another oxygen atom to form superoxide ($O_2^{\ominus}$) ion.

$$\left[O_2^{2-}\ \text{(peroxide)} + \frac{1}{2}O_2 \rightarrow 2O_2^{\ominus}\ \text{(superoxide)}\right]$$

Superoxide ion $[:\ddot{O} \overset{\bullet\bullet\bullet}{\text{—}} \ddot{O}:]^{\ominus}$ has three electron bonds (having one unpaired electron) and is coloured and paramagnetic. For example, LiO_2, NaO_2 are yellow, KO_2 is orange, RbO_2 is brown and CsO_2 is orange. Na_2O_2 (sodium peroxide) is yellow in colour probably due to the presence of a small amount of superoxide in it. The normal oxides of group 1 are however, colourless and diamagnetic.

ILLUSTRATION 1.66

Calculate the ratio of lattice energies of $CaCl_{2(s)}$ and $NaCl_{(s)}$, if the inter-ionic distance in $CaCl_{2(s)}$ is twice that of $NaCl_{(s)}$.

Sol. $r_0\,(NaCl) = r$; $r_0\,(CaCl_2) = 2r$.

$$U_{(NaCl)} \propto \frac{|Z^{\oplus}||Z^{\ominus}|}{r_0} \propto \frac{1\times 1}{r} \propto \frac{1}{r}$$

$$U_{(CaCl_2)} \propto \frac{2\times 1}{2r} \propto \frac{1}{r}$$

$$\therefore \frac{U_{(CaCl_2)}}{U_{(NaCl)}} = 1:1$$

ILLUSTRATION 1.67

a. Give the decreasing order of melting points of the following compounds:
   i. NaF ii. BeO iii. MgO iv. SrO
   Given: The inter-ionic distances in Å as
   NaF = 2.31, BeO = 1.65, MgO = 2.106, SrO = 2.58

b. Give the decreasing order of hardness of the following compounds:
   i. CaO ii. BeO iii. TiC
   Given: The inter-ionic distances in Å as
   CaO = 2.405, BaO = 2.762, TiC = 2.159

Sol.

a. $U_0 \propto \dfrac{|Z^{\oplus}||Z^{\ominus}|}{r_0}$

i. Smaller the inter-ionic distance and high charges on ions, higher the lattice energy and high is the melting point.

ii. Increasing order of inter-ionic distance with same $|Z^{+}| = 2$ and $|Z^{\ominus}| = 2$ is $\overset{+2}{Be}\,\overset{-2}{O} < \overset{+2}{Mg}\,\overset{-2}{O} < \overset{+2}{Sr}\,\overset{-2}{O}$.

iii. Charge in NaF is $|Z^{+}| = 1$, $|Z^{\ominus}| = 1$.

So, the decreasing order of melting point is

BeO > MgO > SrO > NaF (ii > iii > iv > i)

m.pt. (°C) 2930 > 2800 > 2430 > 990

b. i. Higher the lattice energy, higher is the hardness. Charge in $\overset{+4}{Ti}\,\overset{-4}{C}$ is the highest; $|Z^{\oplus}| = 4$, $|Z^{\ominus}| = 4$

ii. Increasing order of inter-ionic distance with same charge, $|Z^{\oplus}| = 2$, and $|Z^{\ominus}| = 2$ is CaO < BaO.

So, the decreasing order of hardness is

	TiC	> CaO	> BaO (iii > i > ii)
	⇓	⇓	⇓
Hardness (in Moh's scale)	8.9	> 4.5	> 3.3

1.27 HYDRATION ENERGY

The amount of energy released when one mole of gaseous ions is dissolved in excess of H_2O to give its constituent aqueous ion, e.g.

$$Na^{\oplus}_{(g)} + aq \longrightarrow Na^{\oplus}_{(aq)}$$

$$Na^{\oplus}_{(g)} + Cl^{\ominus}_{(g)} + aq \longrightarrow Na^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)} \text{ or } NaCl_{(aq)} \qquad \Delta_{Hyd}H^{\ominus} = -ve$$

Generally the hydration energy decreases down the group (↓) and increases along the period (→).

The hydration energy depends on charge density, i.e. $\left(\dfrac{\text{Ionic charge}}{\text{Ionic radius}}\right)$. Greater is the charge density, more easily it attracts the lone pair of oxygen atom in H_2O molecule and more easily it is hydrated and hence more (negative) energy is released. Down the group (↓), charge density decreases and hence hydration energy decreases.

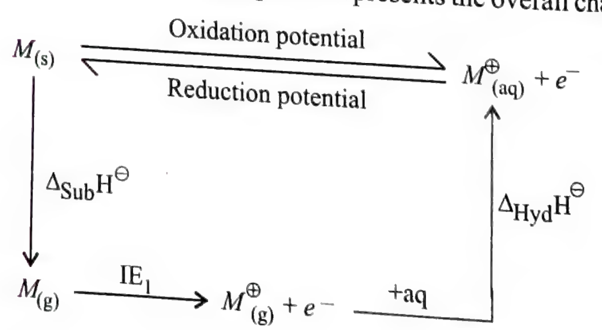
1.27.1 Applications of Hydration Energy ($\Delta_{Hyd}H^{\ominus}$)

1. **Lithium is the strongest reducing agent in aqueous solution:** Because of its very high IE, Li should be the weakest reducing agent. But Li is the strongest reducing agent and Na is the least.

   Reducing character order in aqueous solution is

   Li > Cs > Rb > K > Na

   The standard reduction potential $[E^{\ominus}_{M^{\oplus}(aq)/M(s)}]$ which measures the reducing power represents the overall change.



Due to high charge density $\left(\dfrac{\text{charge}}{\text{size}} \text{ ratio}\right)$, Li has the highest hydration enthalpy which compensates its high IE_1 value, thereby accounts for its high negative $E^{\ominus}$ value and its high reducing power.

$E^{\ominus}_{M^{\oplus}(aq)/M(s)}$ in volts are given for alkali metals as

	Li	Na	K	Rb	Cs
$E^{\ominus}/V$	−3.04	−2.714	−2.925	−2.930	−2.927

2. **Ionic mobilities in electric field of *s*-block ions:** Charge densities of (groups I and 2) ions decrease down the group (↓), so their mobilities in electric field should be in the order:

$Li^{\oplus} > Na^{\oplus} > K^{\oplus} > Rb^{\oplus} > Cs^{\oplus}$

$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

But the observed order of ionic mobilities in aqueous solution is reversed, i.e.

$Cs^{\oplus} > Rb^{\oplus} > K^{\oplus} > Na^{\oplus} > Li^{\oplus}$

$Ba^{2+} > Sr^{2+} < Ca^{2+} > Mg^{2+} > Be^{2+}$

Explanation: $Li^{\oplus}$ and Be^{2+} ions, being heavily hydrated, move very slowly under the effect of electric current and are thus the poorest conductors of electricity as compared to other ions of *s*-block elements. Thus, it is the degree of hydration of ions, rather than their size or charge density that determines the electrical conductivity or ionic mobility of the *s*-block element salt solutions.

3. **Ionic radii in aqueous solution of ions of *s*-block elements:** Smaller the size of a cation, greater is its charge density and hence greater is its tendency to draw electrons from molecules which are thus polarised. Lithium ion and Be^{2+} being the smallest in size among ions of *s*-block elements, they are most extensively hydrated while $Cs^{\oplus}$ and Ba^{2+} ions, the largest ions of *s*-block elements are the least hydrated. So, ionic radii of $Li^{\oplus}$ and Be^{2+} in aqueous solution are the highest and that of $Cs^{\oplus}$ and Be^{2+} ions are the lowest, i.e. the expected relative ionic radii should be

$Cs^{\oplus} > Rb^{\oplus} > K^{\oplus} > Na^{\oplus} > Li^{\oplus}$

$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Be^{2+}$

The observed relative ionic radii in water and relative degree of hydration are reverse of the above order (Fig. 1.15):

Hydrated ions: $Li^{\oplus} > Na^{\oplus} > K^{\oplus} > Rb^{\oplus} > Cs^{\oplus}$

Hydrated radii (Å): 3.40 > 2.767 > 2.32 > 2.28 > 2.27

$\Delta_{Hyd}H^{\ominus}$ (kJ mol^{-1}): –514.7 > –405.9 > –322.2 > –292.9 > –54.4

Hydrated ions: $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ (Group 2)

$\Delta_{Hyd}H^{\ominus}$ (kJ mol^{-1}): –2406 > –1929 > –1632 > –1485 > –1276

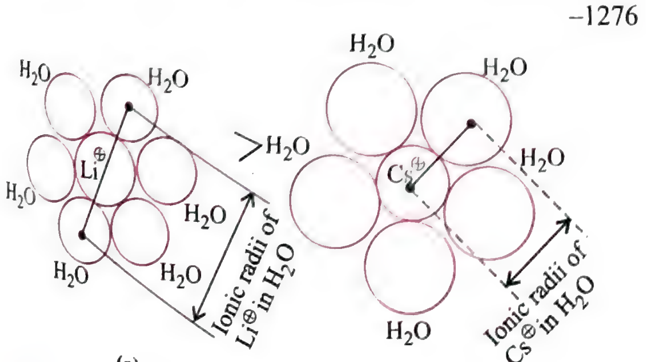


Fig. 1.15 (a) Ionic radii of $Li^{\oplus}$ and (b) Ionic radii of $Cs^{\oplus}$ in H_2O

$Li^{\oplus}$ has maximum degree of hydration and for this reason lithium salts are mostly hydrated (e.g. $LiCl \cdot 2H_2O$) while other alkali metal ions are not hydrated, but NaCl is hygroscopic (absorb moisture).

4. **Reducing nature in aqueous solution of group 2 elements:** Group 2 elements are also strong reducing agent but their reducing power is less than those of their corresponding group 1 elements.

Be is not the strongest reducing agent in group 2 element unlike Li is the strongest reducing agent in group 1 elements.

Reducing power increases down the group (↓) as evident from their $E^{\ominus}_{M^{2+}(aq)/M(s)}$ values.

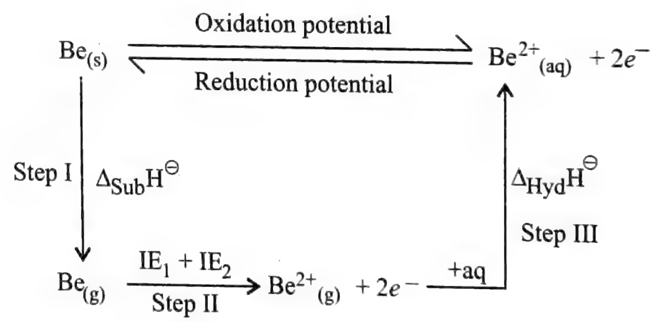
Be has less negative value of $E^{\ominus}_{red}$. compared to other alkaline earth metals, as shown:

Group 2	Be	Mg	Ca	Sr	Ba	Ra
$E^{\ominus}/V$ for $M^{2+}_{(aq)}/M_{(s)}$	–1.97	–2.36	–2.84	–2.89	–2.92	–2.92

Therefore, decreasing order of reducing power in aqueous solution is

Ba > Sr > Ca > Mg > Be

Explanation: The standard reduction potential $E^{\ominus}_{M^{2+}(aq)/M(s)}$, which measures the reducing power represents the over all change.



As a result the overall tendency for the change depends on the net effect of these three steps.

Due to high charge density of Be^{2+} ion, a large amount of hydration energy released in step III does not compensate for the relatively large value of sublimation energy (or atomisation enthalpy) in step I of Be metal plus high (IE_1 +IE_2) value of Be in step II.

Hence, Be is the least reducing agent in aqueous solution among group 2 elements.

5. **Hydrated salt of group 2 elements:** The hydration enthalpies of group 2 metal ions are larger than those of group 1 ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, e.g. $MgCl_2$ and $CaCl_2$ exist as $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$ while LiCl exists as $LiCl \cdot 2H_2O$. NaCl and KCl do not form such hydrates.

6. **Dipositive oxidation state (M^{2+}):** The chemistry of alkaline earth metals is dominated by the dipositive (M^{2+}) oxidation state just as the unipositive ($M^{\oplus}$) oxidation state is the predominant oxidation state of group 1 elements. Alkaline earth metals always form divalent cations.

Explanation: In view of the lower value of first ionisation energy, it would appear that the alkaline earth metals should prefer to form + 1 ions ($M^{\oplus}$ rather than +2 ions e.g. Mg^{2+}, Ca^{2+} etc. If ionisation energy were the only factor involved, we would have got the monovalent ions, i.e. $Mg^{\oplus}$, $Ca^{\oplus}$ etc. rather than the divalent ions, i.e. Mg^{2+} Ca^{2+} etc. But actually we get divalent ions. This anomaly is explained as follows:

a. The +2 ions are extensively hydrated and a large amount of energy known as hydration energy is released in the process which counterbalances the higher value of second ionisation energy. Compared to the heats of hydration (hydration energy) of alkali metal ions of comparable size, the heats of hydration of alkaline earth metal ions are approximately four times greater [e.g. $\Delta_{Hyd}H^{\ominus}$ for $Na^{\oplus}$ (size 102 pm) = – 397 kJ mol^{-1}, $\Delta_{Hyd}H^{\ominus}$ for Ca^{2+} (size 100 pm) = – 1650 kJ mol^{-1}.] The larger hydration energy is due to the fact that the alkaline earth metal ions, because of their much larger charge density, exert a much stronger electrostatic attraction on the lone pairs on the oxygen of water molecule surrounding them.

b. The +2 cations of alkaline earth metals acquire stable inert gas configuration.

7. **Lanthanides and actinides show in general +3 oxidation state:** Their positive high IE_3 value is compensated (or counter balanced) by negative high hydration enthalpies. That is why they generally show +3 OS.

8. **The $E^{\ominus}_{M^{+2}(aq)/M_{(s)}}$ value for copper is postive (+ 0.34 V). Why?**

Explanation : $E^{\ominus}_{(Cu^{+2}\,(aq)/Cu(s))}$ is related to sum of the enthalpy changes taking place as shown below:

$$Cu(s) \xrightarrow[\text{OR } \Delta_{sub}H^{\ominus}]{\Delta_a H^{\ominus}} Cu_{(g)} \xrightarrow{IE_1 + IE_2} Cu^{2+}_{(g)} + 2e^- + aq$$
$$Cu^{2+}_{(aq)} \xleftarrow{\Delta_{Hyd}H^{\ominus}}$$

Copper has high positive enthalpy of atomisation or sublimation enthalpy and low (negative) enthalpy of hydration.

The high energy required to convert $Cu_{(s)}$ to $Cu^{+2}_{(aq)}$ is not compensated by its low hydration energy. Hence, $E^{\ominus}_{Cu^{2+}(aq)/Cu_{(s)}}$ is positive.

9. $Cu^{\oplus}$ compounds are unstable in aqueous solution and undergo disproportionation

$$2\,Cu^{\oplus} \rightarrow 2\,Cu^{2+} + Cu$$

Explanation: The stability of $Cu^{2+}_{(aq)}$ rather than $Cu^{\oplus}_{(aq)}$ is due to the much more negative $\Delta_{Hyd}H^{\ominus}$ of $Cu^{2+}_{(aq)}$ than $Cu^{\oplus}_{(aq)}$, which more than compensates for the IE_2 of Cu.

10. **Solubility in water:**

a. The solubility of a salt in water depends upon (i) lattice energy and (ii) hydration energy.

In general, if hydration energy > lattice energy, salt dissolves. If hydration energy < lattice energy, salt is insoluble.

b. Solubilities in water of hydroxides and fluorides of alkaline earth metal increase down the group (↓).

Explanation: Generally both the lattice and the hydration energy decrease down the group (↓). Lattice energy depends on the comparable size of cations and anions. If sizes of cations and anions are comparable, a strong lattice is formed and a large amount of energy is released.

Alternatively, lattice energy depends on the sizes of the ions whichever is larger.

However, hydration energy depends on the size of the cations or on the charge density (charge/size ratio) of the cations. Smaller is the size or higher the charge density of the cation, more (negative) is the hydration energy, i.e. more energy is released.

Approximate sizes of group 2 ions		**Approximate size of $F^{\ominus}$ ion in fluorides**		**Approximate size of $OH^{\ominus}$ ion in hydroxides**	
Be^{+2}	Size increases ↓	BeF_2	Size of $F^{\ominus}$ ion is constant ↓	$Be(OH)_2$	Size of $OH^{\ominus}$ ion is constant ↓
Mg^{+2}		MgF_2		$Mg(OH)_2$	
Ca^{+2}		CaF_2		$Ca(OH)_2$	
Sr^{+2}		SrF_2		$Sr(OH)_2$	
Ba^{+2}		BaF_2		$Ba(OH)_2$	

Since the sizes of $F^{\ominus}$ and $\overset{\ominus}{OH}$ ions are very small and are not comparable with sizes of any cations. Lattice energy depends on the size of cations which are larger than anions, so lattice energy depends on the size of cations only which increase down the group (↓). Hence, lattice energy decreases more rapidly down the group (↓).

Similarly, charge density of cations i.e. from Be^{2+} to Ba^{2+} also decreases down the group.

But decrease in lattice energy is more than the decrease in hydration energy from Be^{2+} to Ba^{2+}.

In other words, hydration energy > lattice energy.

Hence, solubilities of hydroxides and fluorides of alkaline earth metals increase down the group (↓).

c. Solubilities in water of carbonates, bicarbonates and sulphates of alkaline earth metals decrease down the group (↓).

Explanation: Since the sizes of CO_3^{2-}, $HCO_3^{\ominus}$ and SO_4^{2-} ions are so large and are not comparable with the size of any cations. As we know, lattice energy depends on the size of ions whichever is larger, hence it depends on the size of CO_3^{2-} $HCO_3^{\ominus}$ and SO_4^{2-} ions.

Therefore, the magnitude of lattice energy remains almost constant down the group (↓). As the size of anions are so large

that a small increase in the size of the cations from Be^{2+} to Ba^{2+} does not make any difference.

However, the hydration energy decreases (i.e. from Be^{2+} to Ba^{2+}) appreciably as the size of the cation increases down the group (↓).

In other words, hydration energy < lattice energy. Hence, solubilities of carbonates, bicarbonates and sulphates of alkaline earth metals decrease down the group (↓).

The high solubility of carbonates, bicarbonates and sulphates of Be and Mg is due to their high hydration energies since Be^{2+} and Mg^{2+} ions have smaller size.

Approximate sizes of group 2 ions		**Approximate sizes of CO_3^{2-}; $HCO_3^{\ominus}$ and SO_4^{2-} in their compounds**	
Be^{2+}	Size increases ↓	$BeCO_3$ $Be(HCO_3)_2$ $BeSO_4$	Size of CO_3^{2-}, $HCO_3^{\ominus}$ and SO_4^{2-} ions is constant
Mg^{2+}		$MgCO_3$ $Mg(HCO_3)_2$ $MgSO_4$	
Ca^{2+}		$CaCO_3$ $Ca(HCO_3)_2$ $CaSO_4$	
Sr^{2+}		$SrCO_3$ $Sr(HCO_3)_2$ $SrSO_4$	
Ba^{2+}		$BaCO_3$ $Ba(HCO_3)_2$ $BaSO_4$	

Note: Sizes of CO_3^{2-}, $HCO_3^{\ominus}$ and SO_4^{2-} ions are taken nearly equal only for understanding the concept.

1.28 FLAME COLOURATION

When *s*-block elements or their salts (especially chlorides due to its more volatile nature in a flame) are heated in a bunsen flame, they give characteristic colour in the flame.

Principle: Since the energy of bunsen flame is constant, different elements are excited to different levels due to difference in their IE's

Explanation:

1. When the elements or their salts are heated in a bunsen flame, the electrons of the elements get energy and are excited to higher energy levels. When these excited electrons return to their original (ground) energy level, they emit the same amount of energy as absorbed during excitation in the form of electromagnetic rediation which appears in the visible region of the spectrum, there by imparting a characteristic colour to the flame.

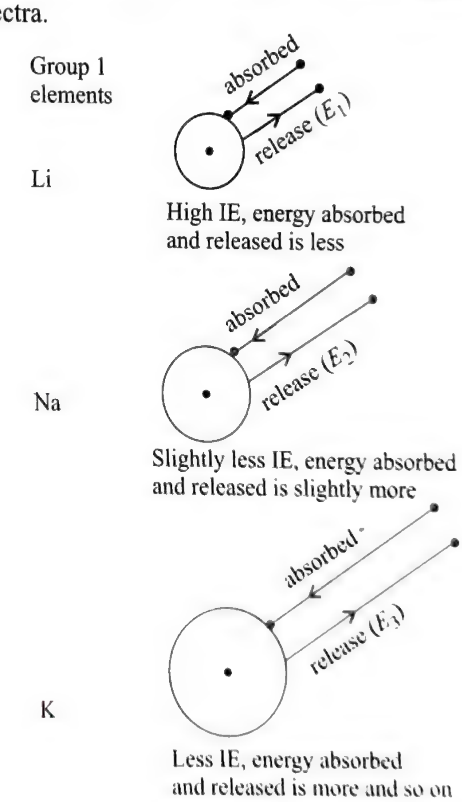
   Thus, the following characteristic colours are given:

Group 1	Li	Na	K	Rb	Cs	
Colour	Crimson	Golden yellow	Violet	Violet	Blue	
λ/nm	670.8	589.2	766.5	780.0	455.5	
Group 2	Be	Mg	Ca	Sr	Ba	Ra
Colour	—	—	Brick red	Crimson	Apple green	Crimson

2. **Flame colouration in alkali metals:** For the same excitation energy, the energy level to which the electron in Li will rise is lower than that to which the electron in Na will rise, this in turn, is lower than the level to which the electron in K will rise and so on. These differences are due to differences in their ionisation energies.

   Consequently, when the electron returns to the ground state, energy released will be lowest in $Li^{\oplus}$ and will increase in the order: $Li^{\oplus}$, $Na^{\oplus}$, $K^{\oplus}$, $Rb^{\oplus}$ and $Cs^{\oplus}$.

   As a result of this, the frequency of light emitted in the bunsen flame is minimum in lithium and corresponds to the red region of visible spectra. In potassium, the frequency of the light emitted corresponds to violet region of visible spectra.



$\therefore \quad E_3 > E_2 > E_1$

(VISIBLE REGION)

V	I	B	G	Y	O	R
K Rb Cs				Na		Li

λ increases →

← Energy increases

3. **Flame colouration in alkaline earth metals:** Be and Mg atoms are smaller in size and have high IE's so their electrons are strongly bonded to the nucleus. They need large amounts of energy for excitation to higher energy levels which is not available in bunsen flame (because energy of bunsen flame is constant), so they do not impart colour to the bunsen flame.

For the same excitation energy, the energy level to which the electrons in Ca will rise is lower than that to which the electrons in Sr will rise, this in turn, is lower than that of the level to which the electrons in Ba will rise and so on.

These differences are due to differences in their IE's.

Consequently, when the electrons return to the ground state, energy released will be lowest in Ca^{2+} ion and will increase in the order.

$$Ca^{2+} < Sr^{2+} < Ba^{2+}$$

As a result of this, the frequency of light emitted is minimum in Ca and corresponds to brick red region of visible spectra. In Ba the frequency of the light emitted corresponds to apple green region of visible spectra.

Cu and Pb and their compounds impart characteristic flame colouration, as

Cu $\Rightarrow$ Deep bluish green

Pb $\Rightarrow$ Pale blue grey

1.29 COLOUR OF A SUBSTANCE IN VISIBLE LIGHT

Most of the transition metal compounds (ionic as well as covalent), halogens and other compounds or ions are coloured in the solid state and in aqueous solution in visible light.

Explanation: Colour of a substance is due to the absorption of light at a specific wavelength in the visible part of the electromagnetic spectrum (400 to 700 nm or 4000 to 7000 Å) and transmission or reflection of the rest of the wavelengths. An object that absorbs all visible light appears black and the object which reflects all visible light appears white.

This means that some of the visible spectrum is being removed from the white light as it passes through the sample, so the light that emerges is no longer white. The colour of the substance is complementary to that which is absorbed.

The complementary colour is the colour generated from the wavelength left over, for example, if blue green light is absorbed by the substance or complex, it appears red.

Table 1.15 (a) gives the approximate (just for understanding) while Table 1.15(b) gives the exact relationship of different wavelength (or colour) absorbed and the complementary colour observed.

Table 1.15(a) Approximate or (theoretical) (for memorising) relationship between the colour absorbed and complementary colour [convert VIBGYOR, YORGVIB]

		Visible spectra					
Colour the light absorbed (VIBGYOR)	V Violet	I Indigo	B Blue	G Green	Y Yellow	O Orange	R Red
Complementary colour (YORGVIB)	Y Yellow	O Orange	R Red	G Green	V Violet	I Indigo	B Blue

Primary colour

400 nm $\quad \lambda \longrightarrow$ increases $\quad$ 700 nm

$\longleftarrow$ Energy (E) increases

Note: Green is a primary colour, hence its absorbed and complementary colour is same

Table 1.15(b) Observed or (exact) relationship between the colour absorbed and the complementary colour

		Visible spectra				
Wavelength and colour of the light absorbed in nm	410 Ultra-violet	475 Blue	498 Blue green	500 Blue green	535 Yellow	600 Red
Complementary colour	Pale Yellow	Yellow orange	Purple	Red	Violet	Blue

Note: Difference between (i) flame colouration and (ii) colour of the substance in visible light.

i. In the first case, the colour is observed in the visible spectra corresponding to the energy released.

ii. In the second case, the observed colour is the complementary colour of the absorbed colour.

1.30 MECHANISM OF ABSORBED COLOUR

When molecules absorb light of a specific wavelength (λ) in the visible region of electromagnetic spectrum, the outer (valence) electrons are excited to higher energy levels. When these excited electrons return to their original (ground) energy levels, they emit radiations in the visible region corresponding to the energy absorbed and gives complementary colour.

Applications

1. **Halogens are coloured:** All halogens are coloured as shown

Halogens	Observed (complementary) colour
$F_{2(g)}$	Yellow
$Cl_{2(g)}$	Greenish yellow
$Br_{2(l)}$	Red or brown or orange
$I_{2(s)}$	Violet

This is due to absorption of radiation in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colour as shown above.

The amount of energy required for excitation decreases progressively down the group (↓), as the IE decreases from F_2 to I_2.

F_2 absorbs violet light (higher excitation energy) and hence gives complementary pale yellow colour while I_2 absorbs yellow and green (lower excitation energy) and appears deep violet. Similarly, greenish yellow colour of Cl_2 and orange red colour of Br_2 can be explained as shown below:

Absorbed colour	V	I	B	G	Y	O	R
Complementary colour	Y	O	R	G	V	I	B
	⇓	⇓	⇓		⇓		
	F_2	Cl_2	Br_2		I_2		

← Energy increases and IE of halogens increases

2. **Blue solution of alkali metals and deep blue black colour of alkaline earth metals in NH_3:** The colour solution of group 1 and group 2 metals in NH_3 is due to the formation of ammoniated metal cations and ammoniated electrons in the metal ammonia solution as

$$M_1 + (x+y)\,NH_3 \longrightarrow [M_1(NH_3)_x]^{\oplus} + [e(NH_3)_y]^{\ominus}$$

$$M_2 + (x+y)NH_3 \longrightarrow [M_2(NH_3)_x]^{2+} + 2[e(NH_3)_y]^{\ominus}$$

where M_1 is the alkali metals and M_2 is the alkaline earth metals.

Explanation:

a. The blue colour of the solution is due to the ammoniated electron which absorbs energy corresponding to red region of visible light and thus imparts complementary blue colour of the solution, as shown

Visible spectrum

Absored colour	V	I	B	G	Y	O	R
Complementary colour	Y	O	R	G	V	I	B

Absorbs energy in red region and gives complementary blue colour.

400 nm ← Energy increases 700 nm

b. The solutions are paramagnetic and has high electrical conductivity due to the presence of unpaired electron or ammoniated electron present in the cavities formed by the electronic polarisation between the electrons and NH_3 molecules. Consequently, the metal solution occupies large volume and has lower density than solvent itself.

c. On standing, the solution slowly liberates $H_{2(g)}$ resulting in the formation of amide.

$$M^{\oplus}_{(am)} + e^- + NH_{3(l)} \longrightarrow MNH_{2(am)} + \frac{1}{2}H_{2(g)}$$

where 'am' denotes solution in NH_3.

d. In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic, due to the formation of metal ion clusters.

In other words, ammoniated metal ions are bound by free unpaired electrons which has been described as 'expanded metals.'

e. However, under anhydrous conditions and in the absence of catalytic impurities such as transition metal ions, solutions can be stored for several days.

3. **The colour in the coordination compounds:** It is explained in terms of crystal field theory (CFT).

Explanation: Colour is due to the presence of incomplete *d*-subshell. Further, when the anions approach the transition metal ions their *d*-orbitals do not remain degenerate. They split into two sets, one with lower energy and the other with higher energy. This is called **crystal field splitting.** Thus, the electrons can jump from lower energy *d*-orbitals to higher energy *d*-orbitals. The required amount of energy to do this is obtained by absorption of the light of a particular wavelength in the region of visible light. One or more electrons from a lower to a higher level within the same *d*-subshell are promoted.

Since the different *d*-orbitals belonging to the same subshell have slightly different energies, the energy required to promote such an electron is very small. Radiations of light corresponding to such small amount of energy are available within the visible light and appear coloured due to emission of the remainder as coloured light.

If a substance absorbs wavelength corresponding to red light the transmitted light will consist of wavelengths corresponding to the complementary colours especially greenish blue colour and the substance will appear greenish blue in colour.

Thus, Cu^{2+} salts look blue due to the absorption of the red wavelength. (Red and greenish blue are said to be complementary colours. Complementary colours are those which when mixed together produce white light.)

Anhydrous cobalt (II) compounds also absorb red light and appear blue. An octahedral complex of titanium $[Ti(H_2O)_6]^{3-}$ is purple in colour. It can be explained on the basis of crystal field theory as follows.

In case of complex ions, *d*-orbitals are split into two different sets due to crystal field effect, one consisting of lower energy orbitals ($d\epsilon$) and the other consisting of higher energy orbitals ($d\gamma$). In $[Ti(H_2O)_6]^{3+}$, Ti has d^1 configuration and this electron is present in t_{2g} orbital in ground state of the complex.

On absorption of yellow green wavelength, the electron is excited to the green next higher state available for the electron is the empty e_g level.

Since the yellow green wavelength is absorbed from the visible region of light it would excite the electron from t_{2g} level to the e_g level ($t_{2g}^1 e_g^0 — t_{2g}^0 e_g^1$). Consequently, the blue and red light will be

transmitted and solution of $[Ti(H_2O)_6]^{3+}$ will appear purple which is the mixed effect of blue and red colours (Fig. 1.16). The CFT attributes the colour of coordination compounds to *d–d* transition of the electron.

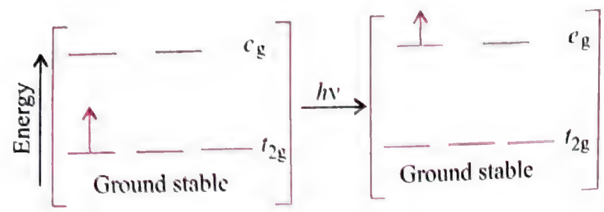


Fig. 1.16 Transition of an electron in $[Ti(H_2O)_6]^{3+}$

Sc^{3+} and Ti^{4+} have completely empty *d*-orbitals and are colourless. $Cu^{\oplus}$ and Zn^{2+} have completely filled *d*-orbitals for promotion of electrons, hence they are also colourless.

In the absence of strong ligand, crystal field splitting does not occur and the substance is colourless.

For example, removal of water from $[Ti(H_2O)_6]\ Cl_3$ on heating renders it colourless. Similarly, $CuSO_4$ is white but $CuSO_4{\cdot}5H_2O$ [i.e.$[Cu(H_2O)_4]^{2+}\ SO_4^{2-}{\cdot}H_2O$] is blue in colour.

In case of a tetrahedral complex, the electron will be excited from lower level, i.e. (*e*) level to the next higher state, i.e. t_2 empty level.

4. **Colour in lanthanides and actinides:** The source of colour in the lanthanides and the actinides is due to *f–f* transitions. In lanthanides, 4*f*-orbitals are deeply embedded inside the atom and are well shielded by the 5*s* and 5*p* electrons. The *f*-electrons are practically unaffected by complex formation, hence the colour remains almost constant for a particular ion, regardless of the ligand.
5. **Colour of some gem stones:** Ruby is Al_2O_3 containing about 0.5–1% Cr^{3+} ions (d^3), which are randomly distributed in positions normally occupied by Al^{3+}. These Cr^{3+} species are octahedral Cr^{3+} complexes incorporated into the alumina lattice; *d–d* transitions at these centres give rise to the colour.
   In emerald, Cr^{3+} ions occupy octahedral sites in the mineral beryl $[Be_3\ Al_2\ Si_6\ O_{18}]$. The absorption bands seen in the ruby shifts to longer wavelength, namely yellow-red and blue, causing emerald to transmit light in the green region.
6. **Colour of compounds having d^o configuration, i.e. *d*-level is empty (charge transfer theory):** In the series Sc^{3+}, Ti^{4+}, V^{5+}, Cr^{6+} and Mn^{7+}, these ions have empty *d*-shell, i.e. d^o configuration, hence *d–d* spectra (or ligand field type) are impossible and they should be colourless.
   However, as the oxidation number increases these states become increasingly covalent. Rather than forming highly charged simple ions, oxoions are formed.
   Examples:
   a. TiO^{2+}, $VO_2^{\oplus}$, VO_4^{3-}, CrO_4^{2-} and $VO_4^{\ominus}$ are pale yellow.
   b. CrO_4^{2-} is strongly yellow coloured.
   c. $MnO_4^{\ominus}$ has intense purple colour in solution though the solid is almost black.
   d. $K_2Cr_2O_7$ has orange colour.

   The colour arises by charge transfer transitions.

   Explanation: As the term implies, these transitions involve electron transfer from part of the complex to another. More specifically, an electron moves from an orbital that is mainly ligand in character to one that is mainly metal in character (i.e. ligand-to-metal charge transfer, LMCT) or vice versa (metal-to-ligand charge transfer, MLCT). Unlike *d–d* transitions, those involving charge transfer are fully allowed and hence give rise to much more intense absorptions. When these absorptions fall in the visible region, they produce complementary colours.

   For example, in $MnO_4^{\ominus}$ an electron is momentarily transferred from oxygen to a metal (LMCT), thus momentarily changing O^{2-} to $O^{\ominus}$ and reducing the oxidation state of the metal from Mn^{7+} to Mn^{6+}. Charge transfer requires that the energy levels on the two different atoms are fairly close and fall in the visible region and produce complementary colour.

   Thus, $KMnO_4$ is purple colour in solution, $K_2Cr_2O_7$ is orange coloured and K_2CrO_4 is yellow in colour, due to charge transfer transitions.

   Many iodide salts are also coloured because of charge transfer transitions. For example, HgI_2 (red), BiI_3 (orange red), PbI_2 (yellow). The metal ions in these substances certainly are not outstanding oxidising agents, but the transitions occur because the $I^{\ominus}$ ion is easily oxidised. Likewise, V_2O_5 is red or orange, $NbCl_5$ is yellow, $NbBr_5$ is orange and NbI_5 is brass coloured.
7. **Compounds of *s*- and *p*-block elements are not coloured:** They do not have a partially filled *d*-shell so there cannot be any *d–d* transitions. The energy to excite an *s* or a *p* electron to a higher energy level is much greater and corresponds to ultraviolet light being absorbed. Thus, the compounds will not be coloured.
8. **Colour due to defects in the solid state:** The colour in solid state is due to the following defects.
   Non-stoichiometric defects: If an imperfection causes the ratio of cations and anions to become different from that indicated by the ideal chemical formula, the defect is called non-stoichiometric. Non-stoichiometric defects are of two types (a) metal excess defects and (b) metal deficiency defects.
   a. **Metal excess defects:** Metal excess defects may occur in either of the following two ways:
      i. **By anion vacancies or F-centre:** Negative ion may be missing from its lattice site, leaving a hole, which is occupied by an electron thereby maintaining an electrical balance. The trapped electrons are called F-centres (from the German word Farbenzenter for colour centres) because they are responsible for imparting colour to the crystal (Fig. 1.17). This defect

is similar to Schottky defect and is found in crystals having Schottky defects.

Example: NaCl when heated in Na vapour atmosphere, the excess Na atom is deposited on the surface. Now $Cl^{\ominus}$ diffuse to the surface where they combine with Na atoms which lose the electrons. The electrons diffuse into the vacant sites created. The electrons absorb some energy from the visible light and re-emit the complementary yellow colour to NaCl crystal. Excess of Li in LiCl gives a pink colour. Excess of K in KCl make it violet.

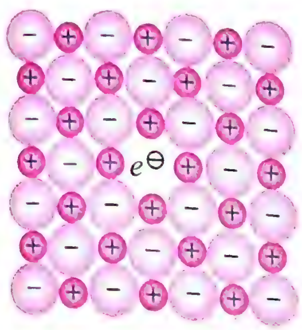


Fig. 1.17 An F-centre in a crystal

ii. **By the presence of extra cations in interstitial sites:** Extra cations occupying interstitial sites with electrons present in another interstitial site to maintain electrical neutrality causes metal excess defects (Fig. 1.18). This defect is similar to Frenkel defect and is formed in crystals having Frenkel defects.

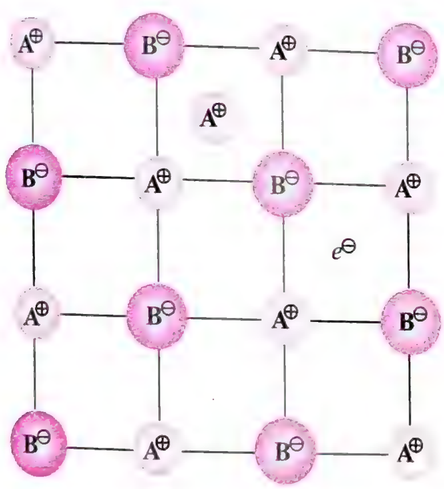


Fig. 1.18 Metal excess defect caused by extra cation in interstitial position

Example: If ZnO is heated, it loses oxygen and turns yellow.

$$ZnO \rightleftharpoons Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Now there is excess of Zn^{2+} in the crystal and its formula becomes $Zn_{(1+x)}O$.

The excess Zn^{2+} ions thus formed get trapped into the vacant interstitial sites, while electrons are entrapped in the neighbouring interstitial sites. These entrapped electrons increase the electrical conductivity of ZnO and turn yellow.

On cooling, they again turn into white due to the reverse reaction as shown above.

Note: Crystals with either type of metal excess defect act as semiconductors.

b. **Metal deficiency defects:** Refer to solid state.

9. Certain substances change their colour when they are hot and revert to their original colour in cold.

Example:

Observation	Compound suspected
a. Yellow when hot and white in cold again	i. ZnO
b. Yellowish brown in hot and yellow in cold	ii. Bi_2O_3 and SnO_2
c. Black or red in hot and brown in cold	iii. Fe_2O_3
d. Yellow in hot and yellow in cold	iv. PbO

ILLUSTRATION 1.68

Identify the complexes which are expected to be coloured.

a. $[Ti(NO_3)_4]$ b. $[Cu(NC\ CH_3)_4]^{\oplus}\ BF_4^{\ominus}$

c. $[Cr(NH_3)_6]^{3+}3Cl^{\ominus}$ d. $K_3[VF_6]$

Sol. (c) and (d) are coloured.

a. $\left[\overset{+4}{Ti}\,\overset{-1\times4}{(NO_3)_4}\right]$; $Ti = 3d^2\,4s^2$, $Ti^{4+} = 3d^0\,4s^0$.

There is no unpaired electron in Ti^{4+} ion, hence no *d–d* transition occurs, so colourless.

b. $\left[\overset{+1}{Cu}\,(NC-CH_3)_4\right]^{\oplus} BF_4^{\ominus}$,

$Cu = 3d^{10}\,4s^1$, $Cu^{\oplus} = 3d^{10}4s^0$

d^{10} configuration of $Cu^{\oplus}$ ion have no unpaired electron, hence colourless.

c. $[Cr^{3+}(NH_3^{\,0})_6]^{3+}$; $Cr = 3d^5\,4s^1$; $Cr^{3+} = 3d^3\,4s^0$.

Cr^{3+} has d^3 configuration, thus have three unpaired electrons, *d–d* transition occurs, hence coloured.

d. $\overset{+1\times3}{K_3}\left[\overset{+3-6}{VF_6}\right]^{-3}$; $V = 3d^3\,4s^2$, $V^{3+} = 3d^2\,4s^0$.

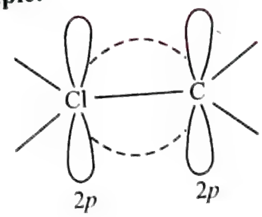
V^{3+} has d^2 configuration, thus have two unpaired electrons, *d–d* transition occurs, hence coloured

1.31 $p\pi$–$p\pi$ MULTIPLE BONDING

First element of groups 14, 15 and 16 shows considerable differences in its chemical properties from that of other members of their respective groups, due to (i) their smaller size, (ii) high IE, (iii) high EN and (iv) non-availability of *d*-orbitals.

Carbon (C), nitrogen (N) and Oxygen (O) have unique ability to form $p\pi$–$p\pi$ multiple bonds with itself and with other elements having (i) small size and (ii) high EN.

Example:



(2p–2p overlap to form $p\pi$–$p\pi$ bond)

$>C=C<$, $-C\equiv C-$, $-C\equiv N$,

$>C=O$ and $>C=S$

$N\equiv N$, $-N=O$, $O=O$ etc.

Heavier elements of these groups do not form $p\pi$–$p\pi$ bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.

Thus, nitrogen exists as a diatomic molecule (N_2) with a triple bond (one s and two p) between the two atoms. Consequently, its bond enthalpy (941.4 kJ mol^{-1}) is very high. On the contrary, phosphorous, arsenic and antimony form single bond as P–P, As–As and Sb–Sb while bismuth forms metallic bonds in elemental state.

However, single N–N bond is weaker than the single P–P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen. Another factor which affects the chemistry of nitrogen is the absence of d-orbitals in its valence shell.

Besides restricting its covalency to four, nitrogen cannot form $p\pi$–$d\pi$ bond as the heavier elements can, e.g. $R_3P = 0$ or $R_3P = CH_2$ (R = alkyl group).

Phosphorous and arsenic can form $d\pi$–$d\pi$ bond also with transition metals when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

Tendency of carbon to form $p\pi$–$p\pi$ multiple bonds is found in the structure of its allotropic modification, graphite.

Elemental silicon exists only in the diamond structure. This clearly indicates the reluctance of silicon to form $p\pi$–$p\pi$ multiple bond.

ILLUSTRATION 1.69

($p\pi$–$p\pi$) back bonding occurs in the halides of boron but not in those of aluminium. Explain.

Sol. The tendency of the central atom (A) in AX_3 molecules (A = B or Al, X = halogens) to form ($p\pi$–$p\pi$) back bonding depends on the size of central atom (A). Smaller is the size of the central atom, greater is the tendency to form ($p\pi$–$p\pi$) back bonding. Since boron (B) atom is smaller in size than aluminium (Al) atom, BX_3 molecules have ($p\pi$–$p\pi$) back bonding while AlX_3 molecules do not have this type of bonding.

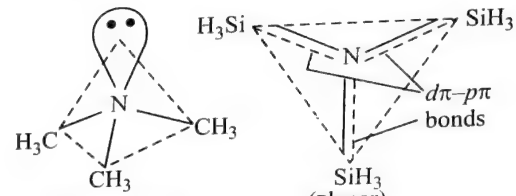
ILLUSTRATION 1.70

The Lewis acid character of boron trihalides decreases as: $BBr_3 > BCl_3 > BF_3$. Explain?

Sol. According to the EN order (F > Cl > B), the Lewis acid character should be $BF_3 > BCl_3 > BBr_3$ but it is observed to be reverse, this can be explained by ($p\pi$–$p\pi$) back bonding that occurs in the given halides.

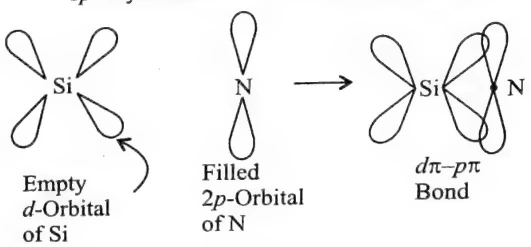
1.32 $p\pi$–$d\pi$ MULTIPLE BONDING

Though the tendency to form $p\pi$–$p\pi$ multiple bonds is not common with silicon and other heavier members of this group, multiple bonding involving d-orbitals has been reported. This tendency is particularly in the case of silicon linked to oxygen and nitrogen. The geometry around the nitrogen atom in trimethylamine $N(CH_3)_3$ is pyramidal (sp^3-hybridisation of nitrogen atom), whereas in the case of similar silicon compound, $N(SiH_3)_3$, called trisilylamine, it is planar arrangement of its three bonds (sp^2 hybridisation of N atom). In the latter case, the lone pair on nitrogen is transferred to the empty d-orbital of silicon ($p\pi$–$d\pi$ overlapping) leading to the planar structure of $N(SiH_3)_3$. For the same reason $N(CH_3)_3$ is more basic than $N(SiH_3)_3$.



(Pyramidal) $N = 2s^2\,2p^3$ sp^3 Hybridisation

(Planar) $Si = 3s^2\,3p^3\,3d^0$ sp^2 Hybridisation



1. All the elements of group 14 form tetrahalides of the formula MX_4, $PbCl_4$ and $PbBr_4$ are unstable and PbI_4 is not known.
2. All these halides are covalent compounds and have tetrahedral shapes.

1.32.1 HYDROLYSIS OF SiX_4

The tetrachloride of carbon (CCl_4) is not hydrolysed by water. However, the tetrachlorides of all the remaining elements are easily hydrolysed.

CCl_4 is not hydrolysed by water because carbon has no d-orbitals and hence cannot expand its coordination number beyond 4. However, silicon can expand its octet (coordination number beyond 4) due to the availability of energetically suitable vacant d-orbitals in its atom.

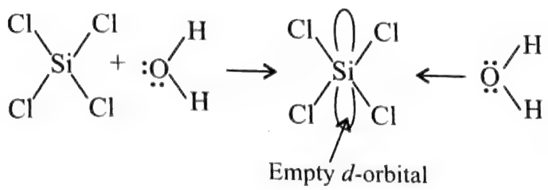
$$CCl_4 + H_2O \longrightarrow \text{No reaction}$$

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{Silicic acid}}{Si(OH)_4} + 4HCl$$

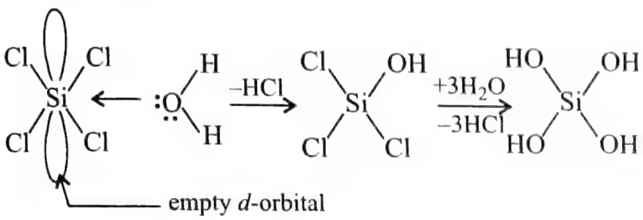
$$SnCl_4 + 2H_2O \longrightarrow SnO_2 + 4HCl$$

The mechanism of hydrolysis of $SiCl_4$ involves two steps:

1. The first step involves the attack of oxygen atom of water molecule on the metal atom forming a coordinate bond between the metal and oxygen atom of water.



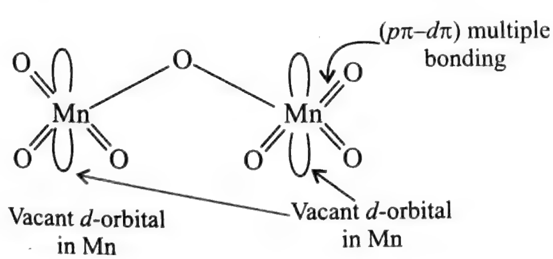
2. The second step involves the loss of HCl. During this step one Cl atom on silicon in $SiCl_4$ is replaced by an OH group. This process continues till all the four Cl atoms are replaced by OH groups yielding $Si(OH)_4$, i.e. silicic acid.



1.32.2 MnF_4 AND Mn_2O_7 EXIST BUT MnF_7 DOES NOT

The highest Mn fluoride is MnF_4, whereas the highest oxide is Mn_2O_7. In other words in Mn fluoride the highest oxidation state of Mn is +4 but in oxides it is +7, although F is more EN than oxygen.

Thus, the ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. This is due to the ability of oxygen to form $p\pi$–$d\pi$ multiple bonds to metals. Vacant 3*d*-orbitals of Mn overlap with 2*p*-orbitals of oxygen to form ($p\pi$–$d\pi$) multiple bonds as shown:



1.33 OXIDES

Properties of representative elements along the period (→) can be compared from the study of the properties of their oxides. The oxides of elements of the 3rd period are Na_2O, MgO, Al_2O_3, SiO_2, P_4O_{10}, SO_3 and Cl_2O_7.

The tendency of oxygen to form oxide ion is greatly favoured when oxygen combines with metals having low IE's such as group 1 and 2 elements, and aluminium (Al). Thus, Na_2O, MgO and Al_2O_3 are ionic compounds having extensive three- dimensional (3D) structures in which each cation is surrounded by a specific number of anions and vice versa. Silicon is a metalloid whose oxide (SiO_2) has a giant 3D network, although no ions are present.

The oxides of P and S and molecular compounds are composed of small discrete units.

1.33.1 PROPERTIES OF OXIDES

Oxygen reacts with almost all elements (except noble gases, Au, Pd, Pt) to form oxides. In general, metallic oxides (O^{2-}), peroxides (O_2^{2-}) and superoxides ($O_2^{\ominus}$) are ionic solids. For example, Li_2O, Na_2O_2 (Na forms peroxide with O_2, rather than oxide), KO_2, RbO_2. The tendency of group 1 metals to form oxygen rich compounds increases upon descending the group, i.e. with increasing cation radii and decreasing charge density on the metal ion. A similar trend is observed in the reaction of group 2 metals. Except Be, group 2 metals react with oxygen at normal conditions to form normal ionic oxides and at high pressure of O_2, they form peroxides (CaO_2, SrO_2, BaO_2).

1. Metals that show variable oxidation states react with a limited amount of oxygen to form lower oxidation state oxides (FeO, Cu_2O) while reacting with an excess of oxygen gives higher oxidation state oxides (Fe_2O_3, CuO).

2. Oxides of metals are called as basic anhydrides as many of them combine with water to form hydroxides with no changes in oxidation state of metals. Oxides of groups 1 and 2 dissolve in water to give basic solutions whereas other oxides are insoluble in water.

3. Oxygen combines with many non-metals to form covalent oxides (such as CO, CO_2, SO_2, SO_3, P_4O_6, Cl_2O_7, N_2O_5 etc.). The reaction of non-metals with a limited amount of oxygen usually gives product that contains non-metals in lower oxidation states, while with excess of oxygen, higher oxidation state oxides are formed. Oxides of non-metals are called **acid anhydrides,** as many of them dissolve in water to form acids and oxyacids. Some of such oxides are as follows:

CO_2, N_2O_5, N_2O_3, P_2O_3, SO_2, SO_3, Cl_2O_7

$CO_2 \rightarrow H_2CO_3$ $\quad Cl_2O_7 \rightarrow HClO_3$ $\quad N_2O_5 \rightarrow HNO_3$

$P_2O_3 \rightarrow H_3PO_3$ $\quad SO_3 \rightarrow H_2SO_4$ $\quad N_2O_3 \rightarrow HNO_2$

$P_2O_5 \rightarrow H_3PO_4$ $\quad SO_2 \rightarrow H_2SO_3$

Note: CO, N_2O, NO and H_2O are neutral oxides.

Table 1.16 Periodic trends in valence of electrons shown by the formula of these oxides

	Group (→) / Period (↓)	1		2	13	14
Formula of oxides	2	Li_2O, oxide		BeO	B_2O_3	CO_2
	3	Na_2O_2 peroxide		MgO	Al_2O_3	SiO_2
	4	KO_2	Super oxides	CaO	Ga_2O_3	GeO_2
	5	RbO_2		SrO	In_2O_3	SnO_2
	6	CsO_2		BaO	–	PbO_2

1.33.2 Classification of Oxides Based on their Chemical Behaviour

Based on their chemical behaviour, the oxides have been classified as:

1. **Acidic oxides:** Oxides which dissolve in water forming acids and neutralise alkalis are called acidic oxides. They are also called acid anhydrides and are generally the oxides of non-metals (e.g. B_2O_3, SiO_2, CO_2, N_2O_3, N_2O_5, P_2O_3, SO_2, SO_3, Cl_2O_7 and I_2O_5 or metallic oxides of high oxidation state (e.g. Mn_2O_7, CrO_3 and V_2O_5)

$$\underset{\text{Sulphur dioxide}}{SO_2} + H_2O \rightarrow \underset{\substack{\text{Sulphurous acid or}\\ \text{Sulphurous anhydride}}}{H_2SO_3}$$

$$\underset{\text{Chromic anhydride}}{CrO_3} + H_2O \rightarrow \underset{\text{Chromic acid}}{H_2CrO_4}$$

2. **Basic oxides:** These may be
   a. **Essentially covalent:** Oxides of transition metals MO and M_2O_3 are essentially covalent. These are non-volatile (giant molecule structure) insoluble in water and not attacked by it.
   b. **Essentially ionic:** These are attacked by water to give alkalis. These are oxides of metals, e.g. Na_2O, CaO, BaO (normal) oxides containing O^{2-} ion); Na_2O_2, BaO_2 (peroxide containing O_2^{2-} ion); and KO_2, RbO_2 (superoxides containing $O_2^{\ominus}$ ion).

$$Na_2O + H_2O \longrightarrow 2\ NaOH$$
$$Na_2O_2 + 2\ H_2O \longrightarrow 2\ NaOH + H_2O_2$$
$$2KO_2 + 2\ H_2O \longrightarrow 2\ KOH + H_2O_2 + O_2$$

3. **Amphoteric oxides:** A few metallic oxides exhibit a dual behaviour. These dissolve in both acids and alkalis.
   a. ZnO gives zinc salts, Zn^{2+} and $Zn(OH)_4^{2-}$.
   b. Al_2O_3 gives aluminium salts, Al^{3+} and aluminates, $Al(OH)_4^{\ominus}$.
   c. SnO gives stannous salts, Sn^{2+} and stannites, $Sn(OH)_4^{2-}$.
   d. SnO_2 gives stannic salts, Sn^{4+} and stannates $Sn(OH)_6^{2-}$.

   The above formulae for hydroxyl complexes are correct for the ions in solution. If the solution, say sodium zincate is evaporated, it loses water.

$$\underset{\text{Zincate}}{ZnO_2^{2-}}\quad \underset{\text{Aluminate}}{AlO_2^{\ominus}};\ \underset{\text{Stannite}}{SnO_2^{2-}};\ \underset{\text{Stamate}}{SnO_3^{2-}}\quad \underset{\text{Plumbite}}{PbO_2^{2-}};\ \underset{\text{Plumbate}}{PbO_3^{2-}}$$

4. **Neutral oxides:** Those oxides which are neutral towards litmus are called neutral oxides. Examples of neutral oxides are carbon monoxide (CO), water (H_2O), nitrous oxide (N_2O) and nitric oxide (NO).

The two systems for classification of oxides are quite independent of each other. For example, sodium oxide (Na_2O) is a **basic oxide as well as normal oxide**. Similarly, nitrous oxide (N_2O) is a **neutral oxide as well as suboxide**.

Examples:

Basic oxides: $Cs_2O > Rb_2O > K_2O > Na_2O > Li_2O > BaO > SrO > CaO > MgO$

Amphoteric oxides: $BeO > Al_2O_3 > Ga_2O_3 > ZnO$ (Table 1.16)

Acidic oxides: $Cl_2O_7 > SO_3 > N_2O_5 > P_2O_5 > CO_2 > B_2O_3$

Group	17	16	15	15	14	13

Neutral oxides: H_2O, CO, N_2O and NO

Table 1.17 Elements forming amphoteric oxides are shown in circles

Acidic character increases →

Basic character increases ↓

s-Block

	1	2
1s		
2s	Li	Be
3s	Na	Mg
4s	K	Ca
5s	Rb	Sr
6s	Cs	Ba
7s	Fr	Ra

H

d-Block

	3	4	5	6	7	8	9	10	11	12
3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5d	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6d	Ac*	Rf	Db	Sg	Bh	Hs	Mt	Ds	Uuu	Uub

p-Block

	13	14	15	16	17	18
						He
2p	B	C	N	O	F	Ne
3p	Al	Si	P	S	Cl	Ar
4p	Ga	Ge	As	Sc	Br	Kr
5p	In	Sn	Sb	Te	I	Xe
6p	Tl	Pb	Bi	Po	At	Rn
7p	–	Uuq	–	Uuh	–	–

1.33.3 Trends of Oxides

1. Trends of oxides in periodic table:

Along the period, oxides show basic to acidic character		
Group	**Example**	**Nature**
1	Na_2O	Strongly basic
2	MgO	Basic
13	Al_2O_3	Amphoteric
14	SiO_2	Weakly acidic
15	P_4O_{10}	Acidic
16	SO_3	Acidic
17	Cl_2O_7	Very strongly acidic

2. In a group, basic nature increases or acidic nature decreases. Oxides of metals are generally basic and oxides of non-metals are acidic. The oxides of metalloids are amphoteric. The oxides of Al, Zn, Sn, As and Sb are amphoteric.

   a. Among *s*-block elements, on moving down a group the basic character increases.

Li_2O	Na_2O	K_2O	Rb_2O, Cs_2O
Weakly basic	Basic	More strongly basic	Very strongly basic

   b. Among *p*-block elements, on moving down the group the acidic character of oxides decreases while the basic character increases. For example in the 13th group, acidic character decreases.

B_2O_3	Al_2O_3	Ga_2O_3	In_2O_3	Tl_2O or Tl_2O_3
Acidic	Amphoteric	Weakly acidic	Basic	Strongly basic

3. In case when an element forms a number of oxides, the acidic nature increases as the percentage of oxygen increases.

Note: For molecules having $\frac{O}{M} \geq 1.5$, they are acidic, others are neutral.

a.

N_2O	NO	N_2O_3	NO_2	N_2O_5
Neutral	Neutral	Acidic	Acidic	Acidic
$\frac{O}{M} = \frac{1}{2} = 0.5$ (Exception)	$\frac{O}{M} = \frac{1}{1} = 1.0$	$\frac{O}{M} = \frac{3}{2} = 1.5$	$\frac{O}{M} = \frac{2}{1} = 2.0$	$\frac{O}{M} = \frac{5}{2} = 2.5$

b.

P_2O_3		P_2O_4		P_2O_5
Acidic		Acidic		Acidic
$\frac{O}{M} = \frac{3}{2} = 1.5$		$\frac{O}{M} = \frac{4}{2} = 2.0$		$\frac{O}{M} = \frac{5}{2} = 2.5$

c.

MnO	Mn_2O_3	MnO_2	MnO_3	Mn_2O_7
Neutral	Neutral	Acidic	Acidic	Acidic
$\frac{O}{M} = \frac{1}{1} = 1.0$	$\frac{O}{M} = \frac{3}{2} = 1.5$ (Exception)	$\frac{O}{M} = \frac{2}{1} = 2.0$	$\frac{O}{M} = \frac{3}{1} = 3.0$	$\frac{O}{M} = \frac{7}{2} = 3.5$

Note: The acidity increases as the oxidation state of N, P or Mn increases to more positive oxidation states.

1.33.4 Classification of Oxides Based on Their Oxygen Content

A binary compound of oxygen with another element is called an oxide. Based on their chemical behaviour or oxygen content, chief classes of oxides are given below:

1. **Normal oxides:** Oxides which contain just as much oxygen as permitted by the normal oxidation number of M are called normal oxides. A few examples of normal oxides are H_2O, MgO, Al_2O_3. These contain only M–O bonds.
2. **Polyoxides:** Oxides containing more oxygen than allowed by normal oxidation number of M are termed as polyoxides. They involve O–O bonds as well as M–O bonds. These have been further classified as given below:

   a. **Peroxides:** These contain O_2^{2-} ion and are derivatives of H_2O_2 (H–O–O–H). These produce hydrogen peroxide with dilute acids and liberate oxygen with concentrated acids. A few examples of true peroxides are sodium peroxide and barium peroxide.

   $BaO_2 + H_2SO_4\,(dil) \rightarrow BaSO_4 + 2\,H_2O_2$

   $2\,BaO_2 + 2\,H_2SO_4\,(conc) \rightarrow 2\,BaSO_4 + 2\,H_2O_2 + O_2$

   b. **Superoxides:** These contain $O_2^{\ominus}$ ion. The superoxides known are KO_2, RbO_2 and CsO_2. These react with water to give hydrogen peroxide and oxygen.

   $2\,KO_2 + 2H_2O \rightarrow 2\,KOH + H_2O_2 + O_2$

   Structure of superoxide: 

   Superoxides have $3\bar{e}$ bond and are paramagnetic and coloured due to the presence of unpaired $\bar{e}$.

   c. **Dioxides:** Polyoxides which contain higher percentage of oxygen such as peroxides but do not give any hydrogen peroxide with dilute acids are termed dioxides. They oxidise conc. HCI to CI_2 and yield O_2 when heated with conc. H_2SO_4. Manganese dioxide (MnO_2) and lead dioxide (PbO_2) are examples of dioxides.

   $2\,MnO_2 + 2\,H_2SO_4\,(conc.) \rightarrow 2\,MnSO_4 + 2\,H_2O + O_2$

   $MnO_2 + 4\,HCI\,(conc.) \rightarrow MnCI_2 + 2\,H_2O + CI_2$

3. **Suboxides:** Oxides which contain a lower percentage of oxygen than expected by the oxidation number of M are called suboxides, e.g. nitrous oxide, N_2O, carbon suboxide (C_3O_2).

   They involve M–M bonds in addition to M–O bonds, for example O = C = C = C = O (carbon suboxide).

4. **Mixed oxides:** Some oxides may be considered to be made of two simpler oxides. Their chemical behaviour confirms this view. These oxides are also called compound oxides, e.g.

a. $\underset{\text{Red lead}}{Pb_3O_4} = \underset{\text{Lead dioxide}}{\overset{+4}{PbO_2}} + \underset{\text{Lead monoxide}}{2\overset{+2}{PbO}}$

b. $\underset{\text{Ferrous ferric oxide}}{Fe_3O_4} = \overset{+2}{FeO} + \overset{+3}{Fe_2O_3}$

c. $\underset{\text{Cobalt aluminate}}{Co(AlO_2)_2} = \overset{+2}{CoO} + \overset{+3}{Al_2O_3}$

d. $Mn_3O_4 = \overset{+4}{MnO_2} + 2\overset{+2}{MnO}$

ILLUSTRATION 1.71

The correct order of relative basic character of NaOH, Mg $(OH)_2$ and $Al(OH)_3$ is

a. $Al(OH)_3 > Mg(OH)_2 > NaOH$
b. $Mg(OH)_2 > NaOH > Al(OH)_3$
c. $NaOH > Mg(OH)_2 > Al(OH)_3$
d. $Al(OH)_3 > NaOH > Mg(OH)_2$

Sol. c. Basic strength decreases along the period (→).

ILLUSTRATION 1.72

Which of the oxides behave both as neutral oxide and suboxide?

a. N_2O **b.** NO **c.** C_3O_2 **d.** CO

Sol.

a. N_2O acts both as neutral oxide and suboxide.
b. NO is neutral oxide.
c. C_3O_2 is suboxide.
d. CO is neutral oxide.

ILLUSTRATION 1.73

Which of the following is not amphoteric oxide?

a. ZnO **b.** BeO **c.** Al_2O_3 **d.** CrO_3

Sol. d. CrO_3 is acidic oxide while others are amphoteric oxide.

ILLUSTRATION 1.74

Which of the following is superoxide?

a. Na_2O_2 **b.** BaO_2 **c.** CsO_2 **d.** MnO_2

Sol. c. CsO_2 is superoxide ($Cs^{\oplus}$ and $O_2^{\ominus}$)
(a) and (b) are peroxide.

ILLUSTRATION 1.75

Which of the oxides is coloured and contains $3e^-$ bond?

a. MgO **b.** Na_2O **c.** KO_2 **d.** Mn_3O_4

Sol. c. KO_2 is superoxide and is coloured and contains $3e^-$ bond.
(a) and (b) are oxides while (d) is mixed oxide of $(2MnO + MnO_2)$.

1.34 PERIODICITY IN HYDRIDES OF ELEMENTS

1. **Hydrides:** Hydrogen forms binary compounds with metals and non-metals and are called hydrides.
2. **Ionic hydrides:** Hydrogen with active metals of groups 1 and 2 forms ionic hydrides. These contain hydride ion $H^{\ominus}$ formed by gaining one electron per atom from an active metal.

   These ionic hydrides are basic in nature as hydride ions reduce water to form $\overset{\ominus}{O}H$ ions and H_2, e.g.

   $LiH_{(s)} + H_2O_{(l)} \longrightarrow LiOH_{(s)} + H_{2(g)}$
   $CaH_2 + 2\,H_2O \longrightarrow Ca\,(OH)_2 + 2\,H_2$
3. The hydrides BeH_2 and MgH_2 are not strongly ionic (intermediate character).

Group (→)	1	2
Period (↓)		
2nd	LiH	BeH_2
3rd	NaH	MgH_2
4th	KH	CaH_2
5th	RbH	SrH_2
6th	CsH	BaH_2

4. **Covalent hydrides:**

   a. These are formed by sharing its electron with an atom of another non-mental to form a single covalent bond.

   b. Hydrogen reacts with non-metals to form binary covalent hydrides

   $$H_2 + X_2\ (\text{halogens}) \longrightarrow 2\,HX_{(g)}$$
   $$3\,H_2 + O_2 \longrightarrow 2\,H_3O$$
   $$3\,H_2 + N_2 \longrightarrow 2\,NH_3$$

   c. Most of the covalent (non-metal) hydrides are acidic in nature. Their aqueous solution produce $H^{\oplus}$ ions in H_2O, e.g. HF, HCl, HI, H_2O, H_2S etc.

1.34.1 Nature of Hydrides

1. The nature of hydrides changes from basic to acidic in a period from the left to the right.

2nd Period	NH_3	H_2O	HF
	Weak base	Neutral	Weak acid
3rd Period	PH_3	H_2S	HCl
	Very weak base	Weak acid	Strong acid

2. In a group, the acidic nature of the hydrides of non-metal increases. The reducing nature also increases but the stability decreases down the group (↓).

1.34.2 Stability of Covalent Hydrides

The stability of the hydrides of groups 13 to 17 decreases down the group (↓) due to corresponding decreases is the strength of

M–H bond as the size of the M atom increases and bond length of M–H bond increases.

Thus, TlH_3, PbH_4, BiH_5 and PoH_2 are quite unstable.

Group (→) Period (↓)		13	14	15	16	17
Period	2	BH_3	CH_4	NH_3	H_2O	HF
	3	AlH_3	SiH_4	PH_3	H_2S	HCl
	4	GaH_3	GeH_4	AsH_3	H_2Se	HBr
	5	InH_3	SnH_4	SbH_3	H_2Te	HI
	6	TlH_3	PbH_4	BiH_3		

1.34.3 Reducing Character of Covalent Hydrides

Since down the group, the stability of hydrides of above group decreases, the ability to give H-atom increases (i.e. ability of oxidation increases). Thus, the heavier hydrides have more reducing character.

In other words, the reducing character of the hydrides of the above group increases down the group (↓).

ILLUSTRATION 1.76

The least stable hydride is

a. Stannane **b.** Silane **c.** Plumbane **d.** Germane

Sol. **c.** Stability order of carbon family hydride is Silane (SiH_4) > Stannane (SnH_4) > Plumbane (PbH_4)

Hence the answer is (c).

ILLUSTRATION 1.77

The most stable hydride is

a. B_2H_6 **b.** AlH_3 **c.** GaH_3 **d.** InH_3

Sol. **a.** BH_3 or B_2H_6 is the most stable since the stability of hydrides decreases down the group (↓).

ILLUSTRATION 1.78

The strongest reducing hydride is

a. NH_3 **b.** PH_3 **c.** AsH_3 **d.** SbH_3

Sol. Reducing character of hydrides increases down the group (↓).

CONCEPT APPLICATION EXERCISE 1.2

1. Why inert gases are monoatomic?
2. Potassium (K) is strongly metallic, while Cl is strongly non-metallic. Explain.
3. Why metals are good conductors of electricity?
4. Comment on 'Iodine possesses some metallic lusture'.
5. Of all noble metals, gold (Au) has a relatively high EA. Explain.
6. In alkali metal which element is the strongest reducing agent in aqueous solution and why?
7. Cl can be converted to $Cl^{\ominus}$ ion easily than F to $F^{\ominus}$ ion. Explain.
8. Why Be and Mg do not impart flame colouration?
9. The IE of K is same as EA of $K^{\oplus}$ ion. Explain.
10. Explain the large atomic radii of noble gases.

1.35 ARRHENIUS CONCEPT OF ACIDS AND BASES

According to this concept, an acid and a base can be defined as follows:

Acid: It is a substance that produces hydrogen ions ($H^{\oplus}$) in water, e.g. HCl, H_2SO_4, HNO_3 etc.

Base: It is a substance that produces hydroxyl ion ($\overset{\ominus}{O}H$) in water. NaOH, KOH, $Mg(OH)_2$ etc. are the examples of Arrhenius bases.

Let us represent an acid as HX and a base as BOH.

The ionisation of acid as (HX) can be represented by the following equation:

$$HX_{(aq)} + H_2O_{(l)} \longrightarrow \underset{\text{(hydronium ion)}}{H_3O^{\oplus}_{(aq)}} + X^{\ominus}_{(aq)}$$

or simply, $HX_{(aq)} \longrightarrow H^{\oplus}_{(aq)} + X^{\ominus}_{(aq)}$

Hydronium ion ($H_3O^{\oplus}$) is used to represent a hydrated $H^{\oplus}$ ion. i.e. $H^{\oplus}$ ion surrounded by water molecules.

General formula of a hydronium ion is $H_{2n+1}O_n^{\oplus}$.

Thus, $H_9O_4^{\oplus}$ is a hydronium $H^{\oplus}$ ion surrounded by four water molecules.

1. $H_3O^{\oplus} + H_2O \longrightarrow H_5O_2^{\oplus}$
2. $H_5O_2^{\oplus} + H_2O \longrightarrow H_7O_3^{\oplus}$
3. $H_7O_3^{\oplus} + H_2O \longrightarrow H_9O_4^{\oplus}$

Similarly, the ionisation of a base (BOH) is represented by the following equation:

$$BOH_{(aq)} + H_2O_{(l)} \longrightarrow B^{\oplus}_{(aq)} + H_3O_2^{\ominus}{}_{(aq)}$$

or simply: $BOH_{(aq)} \longrightarrow B^{\oplus}_{(aq)} + \overset{\ominus}{O}H_{(aq)}$

The hydroxyl is hydrated to give species of general formula $H_{2n-1}O_n^{\ominus}$.

1. $\overset{\ominus}{O}H + H_2O \longrightarrow H_3O_2^{\ominus}$
2. $H_3O_2^{\ominus} + H_2O \longrightarrow H_5O_3^{\ominus}$
3. $H_5O_3^{\ominus} + H_2O \longrightarrow H_7O_4^{\ominus}$

Note: The Arrhenius concept of acids and bases is only limited to aqueous solutions.

1.35.1 Limitations of Arrhenius Concept

1. It is applicable only to the aqueous solutions. For the acidic or basic properties, the presence of water is absolutely necessary. Dry HCl shall not act as an acid.

2. The concept does not explain the acidic or basic properties of acids or bases in non-aqueous solvents respectively.
3. It fails to explain the acidic nature of the non-protic compounds such as SO_2, NO_2, CO_2, P_2O_5 etc., which do not have hydrogen for furnishing $H^{\oplus}$ ions.
4. It fails to explain the basic nature of compounds such as NH_3, Na_2CO_3 etc., which do not have OH in the molecules to furnish $\overset{\ominus}{O}H$ ions.
5. It fails to explain the acidic nature of certain salts such as $AlCl_3$ in aqueous solution.

1.36 BRONSTED–LOWRY ACIDS AND BASES

According to this concept, an acid and a base can be defined as follows:

Acid: It is a substance that can donate a proton.

Base: It is a substance that can accept a proton.

Example: When HCl is dissolved in water, it donates a proton to H_2O which behaves as a base.

$$HCl_{(aq)} + H_2O_{(l)} \longrightarrow Cl^{\ominus}_{(aq)} + H_3O^{\oplus}_{(aq)}$$

Other examples of Bronsted–Lowry acids (underlined) are:

1. $\underline{NH_4^{\oplus}}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^{\oplus}_{(aq)}$
2. $\underline{HSO_4^{\ominus}}_{(aq)} + H_2O_{(l)} \rightleftharpoons SO_4^{2-}{}_{(aq)} + H_3O^{\oplus}_{(aq)}$
3. $\underline{HCl}_{(aq)} + NH_{3(aq)} \rightleftharpoons Cl^{\ominus}_{(aq)} + NH_4^{\oplus}{}_{(aq)}$
4. $\underline{HCO_3^{\ominus}}_{(aq)} + NH_{3(aq)} \rightleftharpoons CO_3^{2-}{}_{(aq)} + NH_4^{\oplus}{}_{(aq)}$

Some examples of Bronsted–Lowry bases (underlined) are:

1. $\underline{O^{2-}}_{(aq)} + H_2O_{(l)} \rightleftharpoons \overset{\ominus}{O}H_{(aq)} + \overset{\ominus}{O}H_{(aq)}$
2. $\underline{NH_3}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^{\oplus}{}_{(aq)} + \overset{\ominus}{O}H_{(aq)}$
3. $\underline{CO_3^{2-}}_{(aq)} + H_2O_{(l)} \rightleftharpoons HCO_3^{\ominus}{}_{(aq)} + \overset{\ominus}{O}H_{(aq)}$

Note:

i. This theory states that an acid must contain transferable hydrogen and it offers great freedom in defining what constitutes a base.

ii. When an acid has donated its proton, the remaining portion of the molecule or ion is a base.

iii. When a base accepts a proton, it forms an acid.

iv. The base must have an unshared pair of electrons so as to accept a proton.

The base formed from an acid is known as the *conjugate base of the acid.* Correspondingly, the acid formed from a base is called the *conjugate acid of the base.*

$$\underset{Acid_1}{HCl} + \underset{Base_2}{NH_3} \rightleftharpoons \underset{Base_1}{Cl^{\ominus}} + \underset{Acid_2}{NH_4^{\oplus}}$$

In the above reaction, $Cl^{\ominus}$ is the conjugate base of HCl and $NH_4^{\oplus}$ is the conjugate acid of NH_3.

Note:

i. The conjugate acid always has one or more proton than its conjugate base.

ii. To obtain a conjugate acid of a compound, remove a proton ($H^{\oplus}$) from it and to obtain the conjugate base of the same, add a proton to the compound, e.g. conjugate acid of NH_3 is $NH_4^{\oplus}$ while the conjugate base of NH_3 is $NH_2^{\ominus}$.

iii. This concept has the advantage that it can be applied to a solvent other than water, having the tendency to accept or lose a proton.

iv. The terms acid and base are comparative. A substance can behave as an acid in one solvent and as a base in another.

For example, acetic acid (CH_3COOH) behaves as an acid in water and as a base in HF.

$$\underset{Acid}{CH_3COOH_{(aq)}} + \underset{Base}{H_2O_{(aq)}} \rightleftharpoons CH_3COO^{\ominus}_{(aq)} + H_3O^{\oplus}_{(aq)}$$

$$\underset{Base}{CH_3COOH_{(aq)}} + \underset{Acid}{HF_{(aq)}} \rightleftharpoons CH_3COOH^{\oplus}_{2(aq)} + F^{\ominus}_{(aq)}$$

1.36.1 Strength of Bronsted–Lowry Acids and Bases

The strength of an acid or a base is measured by its tendency to lose or gain proton. A strong acid is a substance which loses a proton easily to a base. Consequently, the conjugate base of a strong acid is a weak base.

$$\underset{(Strong\ acid)}{HCl} + H_2O \longrightarrow \underset{(Weak\ base)}{Cl^{\ominus}} + H_3O^{\oplus}$$

$$\underset{(Weak\ acid)}{HS^{\ominus}} + H_2O \rightleftharpoons H_3O^{\oplus} + \underset{(Strong\ base)}{S^{2-}}$$

The ability of an acid to lose proton is experimentally measured by its equilibrium constant known as K_a.

The larger the value of K_a, the more complete a reaction or higher the concentration of $H_3O^{\oplus}$ and the stronger is the acid.

Similarly, for bases, we have the equilibrium constant K_b which determines the extent of the completion of the reaction.

Reaction of common ions with water:

No reaction	Weak reaction	Strong reaction
	Basic	
$Cl^{\ominus}$, $Br^{\ominus}$, $I^{\ominus}$ $NO_3^{\ominus}$, $ClO_4^{\ominus}$	$CH_3COO^{\ominus}$, $F^{\ominus}$, $NO_2^{\ominus}$, $HCO_3^{\ominus}$, $CN^{\ominus}$, SO_4^{2-}, SO_3^{2-}	PO_4^{3-}, S^{2-}, CO_3^{2-}
	Acidic	
$Li^{\oplus}$, $Na^{\oplus}$, $K^{\oplus}$ Mg^{2+}, Ca^{2+}, $Ag^{\oplus}$	$NH_4^{\oplus}$, Be^{2+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Sn^{2+}, Cd^{2+}	Fe^{3+}, Bi^{3+}, Sn^{4+}, Al^{3+}

Note: In general, solvents can be of four types:

i. **Protophilic:** Solvents having a tendency to accept protons. For example, water, alcohol, liquid ammonia etc.

ii. **Protogenic:** Solvents having a tendency to donate protons. For example, water, liquid HF, liquid HCl etc.

iii. **Amphiprotic:** Solvents having a tendency to accept or donate protons. For example, water, liquid ammonia etc.

iv. **Aprotic:** Solvents which neither accept nor donate protons. For example, benzene, carbon tetrachloride etc.

1.36.2 Amphoteric Compounds

The compounds which can act either as acids or as bases. H_2O, NH_3 and CH_3COOH are some of the examples.

1. **Water:** $\underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{NH_3} \rightleftharpoons \overset{\ominus}{O}H + NH_4^{\oplus}$

$$\underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{H_2O} \rightleftharpoons H_3O^{\oplus} + \overset{\ominus}{O}H$$

In the first reaction, H_2O is behaving as an acid while in the second one it is behaving as a base.

2. **Bicarbonate:** $HCO_3^{\ominus} + NH_3 \rightleftharpoons \underset{\text{Acid}}{CO_3^{2-}} + \underset{\text{Base}}{NH_4^{\oplus}}$

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{HCO_3^{\ominus}} \rightleftharpoons Cl^{\ominus} + H_2CO_3$$

Note: The reaction $H_2O + H_2O \rightleftharpoons H_3\overset{\oplus}{O} + \overset{\ominus}{O}H$ is known as auto-ionisation of water.

1.36.3 Limitations of Bronsted Concept

1. A substance is termed as an acid or a base if it reacts with some other substance, i.e. if it donates proton to other substance, it is an acid and if it accepts proton from other substance, it is a base.
2. There are a number of acid–base reactions in which no proton transfer takes place, e.g.

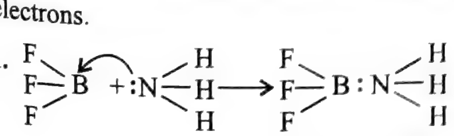
$$\underset{\text{Acid}_1}{SO_2} + \underset{\text{Base}_2}{SO_2} \rightleftharpoons \underset{\text{Acid}_2}{SO^{2+}} + \underset{\text{Base}_1}{SO_3^{2-}}$$

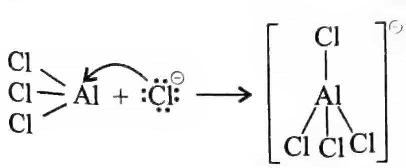
Thus, the protonic definition cannot be used to explain the reactions occurring in non-protonic solvents such as $COCl_2$, SO_2, N_2O_4 etc.

1.37 Lewis Acids and Bases

Acid: It is a substance that can form a bond by accepting a shared pair of electrons.

Base: It is a substance that possesses at least one unshared pair of electrons.

1. 

2. 

Monoprotic acids: Acids that give up one proton per molecule.

Polyprotic acids: Acids that can give up more than one proton per molecule.

Substances that are bases in the Bronsted system are also bases according to the Lewis concept. However, the Lewis definition of an acid considerably expands the number of substances that are classified as acids. A Lewis acid must have an empty orbital capable of receiving the electron pair of the base.

Lewis acids include molecules or atoms that have incomplete octets. For example, molecules such as BF_3, $AlCl_3$ etc. act as Lewis acid.

Many simple cations can act as Lewis acids:

$$Cu^{2+} + 4\ddot{N}H_3 \longrightarrow [Cu(NH_3)_4]^{2+}$$

$$Fe^{3+} + 6\,(:C \equiv N:)^{\ominus} \longrightarrow [Fe(C \equiv N)_6]^{3-}$$

Some metal atoms can function as acids in the formation of compounds such as

$$Ni + 4\,C \equiv O \longrightarrow Ni(CO)_4$$

Compounds that have central atoms capable of expanding their valence shells are Lewis acids in reaction in which this expansion occurs.

$$SnCl_4 + 2Cl^{\ominus} \longrightarrow SnCl_6^{2-}$$

$$SiF_4 + 2F^{\ominus} \longrightarrow SiF_6^{2-}$$

$$PF_5 + F^{\ominus} \longrightarrow PF_6^{\ominus}$$

Some compounds have an acidic site because of one or more multiple bonds in the molecule.

1.38 OXYACIDS

Acids that contain oxygen are called oxyacids.

Acidity of oxyacids increases with increasing oxidation number of the central atom, the atom to which oxygen atoms are attached.

Acid	Formula	Oxidation number of chlorine
Hypochlorous	HClO	+1
Chlorous	$HClO_2$	+3
Chloric	$HClO_3$	+5
Perchloric	$HClO_4$	+7

Due to resonance, the electron density decreases as the number of oxygen atoms in the oxyacids increases.

Note:

i. For monatomic anions of similar charge, base strength decreases with increasing size.
For example, S^{2-} is a weaker base than O^{2-} as the size of S^{2-} ion is greater than that of O^{2-}.
(Consequently, H_2S is a stronger acid than H_2O.)

ii. The base strength of anions is also influenced by the charge on them.
Thus, the base strength of the monatomic anions of the elements of the second period $N^{3-} > O^{2-} > F^{\ominus}$ decrease with increasing EN and with decreasing negative charge on the ion.

iii. For acids with structure: H – O – Z, the acid strength increases with increasing EN of Z.

The higher the EN of Z, the more the electrons of the molecule are displaced toward Z and the more proton is removed.

However, for the oxyacids of phosphorus, the oxidation number fails to give a true indication of the acid strength.

Thus, H_3PO_2, H_3PO_3 and H_3PO_4 are approximately of equal strength although the oxidation state of P in these three oxyacids are +1, +3 and +5 respectively.

The number of O atom bonded to the central atom but not bonded to H atoms influence the formal charge of the central atom and thus provides a qualitative indication of the strength of acids of the general formula $(HO)_x ZO_y$ (x and y are positive integers).

$HOCl < HOClO < HOClO_2 < HOClO_3$

or $HClO < HClO_2 < HClO_3 < HClO_4$

For the variations in the same groups (i.e. compounds with x and y), the acidic character increases with increasing EN of the central atom.

$HClO_3 > HBrO_3 > HIO_3$

1.38.1 Strength of Binary Acids and Oxyacids

They are composed of hydrogen and a non-metallic elements.

Increasing acidity →

CH_4	NH_3	H_2O	HF
		H_2S	HCl
		H_2Se	HBr
			HI

Increasing acidity ↓

The following factors influence the acid strength:

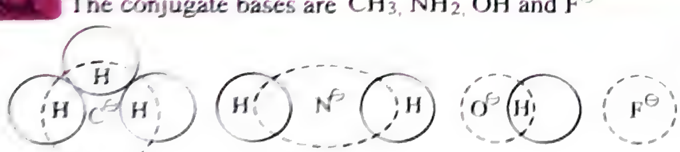
1. Too many factors influence the acid strength, making the predictions impossible.
2. The acid strength order will be explained on one main assumption of charge density.
3. Basicity of an ion is related to the volume available to the electron, i.e. the volume over which the electron can spread. The greater the volume available for a given series of basic ions, the smaller is the electron density. The smaller the electron density, the smaller is the attraction for the proton and weaker the base. The weaker the base, the stronger is the conjugate acid.

Illustration 1.79

Arrange the following acids in the decreasing order of their acid strength:

CH_4, NH_3, H_2O, HF

Sol. The conjugate bases are $\overset{\ominus}{C}H_3$, $\overset{\ominus}{N}H_2$, $\overset{\ominus}{O}H$ and $F^{\ominus}$



Nearly 3/4th of the volume of C is overlapped by H-atoms	Half of the volume of N is overlapped by H-atoms	Less than half the volume of O is overlapped by H-atoms

Increasing volume available to electron →

Decreasing electron density →

Decreasing electron donating tendency →

Decreasing basicity of conjugate bases →

Increasing acidity of corresponding acids →

$\therefore$ $HF > H_2O > NH_3 > CH_4$

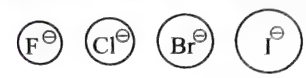
Illustration 1.80

Arrange the following acids in the decreasing order of their acid strength:

HF, HCl, HBr, HI

Sol. $F^{\ominus}$, $Cl^{\ominus}$, $Br^{\ominus}$ and $I^{\ominus}$ are the conjugate bases of HF, HCl, HBr and HI respectively.

Sizes of conjugate bases are as shown:



Increasing volume available to electron →

Decreasing electron density →

Decreasing electron donating tendency →

Decreasing basicity of conjugate bases →

Increasing acidity of corresponding acids →

$\therefore$ $HI > HBr > HCl > HF$

1.39 Trends in Acidic and Basic Properties Based on Arrhenius and Bronsted–Lowry Concepts

1. **Covalent hydrides:** In these the proton is directly attached with the central atom of the molecule.

   HX (X = F, Cl, Br, I), H_2O, CH_4, H_2S etc. These are also called hydracids or hydroacids.

   Two factors influence the acid strength of the hydride of an element are the EN of the element and the atomic size of the element. The first of these factors is best understood by comparing the hydrides of the elements of a period of the periodic table. The second is important when group comparisons of the periodic table are made.

   a. **Hydrides of the element of a period:** The acid strengths of the hydrides of the elements of a period increase from the left to the right in the same order as EN increases. Highly EN element withdraws electrons from the hydrogen easily and facilitate the release of hydrogen as proton. The EN of the following second and third period elements fall in the order: F > O > N and Cl > S > P.

The acid strength of the hydrides increases in the same order: $NH_3 < H_2O < HF$ and $PH_3 < H_2S < HCl$.

The increase in acidic nature is also due to the fact that the solubility of their conjugate bases increases in the order: $NH_2^{\ominus} < \overset{\ominus}{O}H < F^{\ominus}$.

The increase in the acidic properties is supported by successive increase in the dissociation constant.

$NH_3\ (=10^{-35}) < H_2O\ (=10^{-14}) < HF\ (=10^{-4})$

b. **Hydrides of the elements of a group:** The acidity of the hydrides of the elements of group increases with increasing size of the central atom. For example, in the hydrides of groups 16 and 17, the acidic nature increases as the atomic number of the central element increases.

$H_2O < H_2S < H_2Se < H_2Te$ and $HF < HCl < HBr < HI$

The two factors which influence acid strength work against each other in these hydrides. The effect of atomic size outweighs the electronegativity effect. A proton is more easily removed from a hydride in which the central atom is large than from the one in which the central atom is small. The charge density on the conjugate base is in the order:

$O^{2-} > S^{2-} > Se^{2-} > Te^{2-}$ and $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

Greater charge density on the conjugate base will result in greater proton attraction.

The acidic nature of the hydrides of group 17 elements is also explained by the fact that bond energies decrease.

H–F	>	H–Cl	>	H–Br	>	H–I
135 kcal mol^{-1}		103 kcal mol^{-1}		88 kcal mol^{-1}		71 kcal mol^{-1}

Due to large electronegativity, hydrogen bonding exists in the hydrides of oxygen and fluorine which also decrease their acid strength.

In the hydrides of the elements having nearly the same electronegativity, the acidic nature increases as the size of the central element increases. C, S and I possess same electronegativity, the acidic nature follows the following order:

$CH_4 < H_2S < HI$ as the size increases from carbon to iodine.

2. **Oxyacids:** In these the proton is attached to an oxygen atom, the latter being bonded to the central atom. For example, H_2SO_3, HNO_3, H_2SO_4, $HClO_4$ etc.

$H-O-Z$

The main factors which affect the strength of an oxyacid are

a. The size of the central atom
b. The electronegativity of the central atom
c. The number of other electronegative atoms attached to the central atom

Smaller the size and greater the electronegativity of Z make the oxyacid stronger. These factors will shift the electron pair between Z and O towards Z and this displacement will in turn cause a shifting of electron pair between oxygen and hydrogen towards oxygen. Thus, O–H bond is weakened and proton is easily released in the series, HOI < HOBr < HOCl.

The electronegativity increases and size decreases of the central element. Same trend is observed in the oxyacid of different elements in the same oxidation state $HClO_4 > HBrO_4 > HIO_4$.

Greater the number of negative atoms present in the oxyacid make the acid stronger. In general, the strengths of acids that have general formula $(HO)_xZO_y$ can be related to the value of y.

If $y = 0$, the acid is very weak. HOCl, $(OH)_3B$ or H_3BO_3, $(OH)_4Si$ or H_4SiO_4.

If $y = 1$, the acid is weak, HOClO, HONO, $(HO)_2SO$, $(HO)_2SO_2$.

If $y = 2$, the acid is strong, $HClO_2$, $HONO_2$, $(HO)_2SO_2$.

If $y = 3$, the acid is very strong, $HClO_3$, $HOIO_3$.

The negative atoms draw electrons away from the Z-atom and make it more positive. The Z-atom, therefore, becomes more effective in withdrawing electron density away from the oxygen atom that is bonded to hydrogen. In turn, the electrons of H–O bond are drawn more strongly away from the H-atom. The net effect makes it easier for the proton release and increases the acid strength.

This effect is illustrated by the following series of acids:

$$HO\overset{+1}{Cl} < HO\overset{+3}{Cl}O < HO\overset{+5}{Cl}O_2 < HO\overset{+7}{Cl}O_3$$

$$H_2\overset{+4}{S}O_3 > H_2\overset{+4}{S}O_4 : H\overset{+3}{N}O_2 > H\overset{+5}{N}O_3$$

Note: In the above examples, it is evident that strength of the acid increases as the oxidation number of the central atom increases. However, this rule fails in oxyacids of phosphorus.

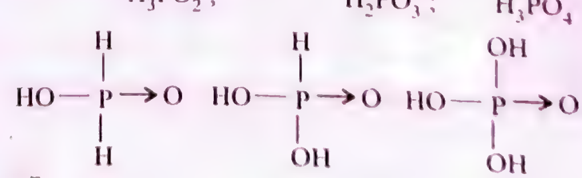
$$H_3\overset{1+}{P}O_2 : H_3\overset{3+}{P}O_3 : H_3\overset{5+}{P}O_4$$

As all are weak acids, i.e. about the equal strength. Thus, prediction on the basis of oxidation number is incorrect. Formal charge on the central atom gives more reliable prediction. The strength of the acid increases as the formal charge on the central atom increases.

Formal charge = [Group number – number of bonds – number of unshared electrons.]

Formal charge on Cl	HOCl	< HOClO	< $HOClO_2$	< $HOClO_3$
	0	+1	+2	+3

H_3PO_2 ; H_3PO_3 ; H_3PO_4



Formal charge on P	+1	+1	+1

As the formal charge is same, all the above oxyacids of phosphorus are nearly of equal strength.

1.39.1 STRENGTH OF BASES

1. Among alkali and alkaline earth metal oxides and hydroxides, the basic nature increases as the size of the central atom increases, i.e. electropositive nature increases.

   CsOH > RbOH > KOH > NaOH >LiOH

   $Ba(OH)_2 > Sr(OH)_2 > Ca(OH)_2 > Mg(OH)_2 > Be(OH)_2$

2. Among the hydrides of the same group, the basic nature decreases with increase in the size of central atom as the tendency to accept proton decreases due to decrease in electron density (or ability to donate electron pair decrease).

   $\underset{\text{Basic}}{NH_3} > \underset{\text{Less basic}}{PH_3} > \underbrace{AsH_3 > SbH_3 > BiH_3}_{\text{Netural}}$

3. The larger the size of the atom holding the unshared electrons, the lesser is the availability of the electrons, i.e. the basic strength of halide ions follow the following order:

   $\underset{\text{Smaller size}}{F^{\ominus}} > Cl^{\ominus} > Br^{\ominus} > \underset{\text{Larger size}}{I^{\ominus}}$

   Similarly, $O^{2-} > S^{2-} > Se^{2-} > Te^{2-}$

4. The basic nature of a substance decreases with the increase of the electronegativity of the atom holding the lone pair of electrons, i.e. the tendency to donate the electron pair to proton decreases with increase of electronegativity

   $NH_3 > H_2O > HF$

5. The presence of a positive charge on the atom holding the lone pair decreases the base strength while a negative charge increase the base strength.

   $\overset{\ominus}{O}H > H_2O > H_3O^{\oplus}$

6. Base strength increases with decrease in oxidation state of the central atom.

   $NH_3 > N_2H_4 : PH_3 > P_2H_4$

   Oxidation number $-3 \quad -2 \quad -3 \quad -2$

1.40 SOFT AND HARD ACIDS AND BASES

Lewis acids and bases are classified as hard and soft acids and bases. A firmly held electron cloud with low polarisability makes a species 'hard', whereas an easily polarisable electron cloud characterises the species as 'soft'. A third category with intermediate character appears in the border line. Thus, we have the following cases:

1. **Hard acid:** Those species in which the electron-accepting atom is small with a high positive charge and there are no electrons which are easily polarised or removed.
2. **Soft acid:** Those species in which the acceptor atom is large, carries a low positive charge or has electrons in orbitals which are easily polarised or distorted.
3. **Hard base:** The Lewis base which holds its electrons strongly.
4. **Soft base:** The Lewis base in which the position of the electrons is easily polarised or removed.
5. **SHAB (soft and hard acid base) principle:** Soft bases (nucleophiles) bind best with soft acids (electrophiles) and hard bases with hard acids. This is known as SHAB principle.

   The smallest $M^{\oplus}$ is the 'hardest' acid and smallest $X^{\ominus}$ is the hardest base. They combine to form the strongest bonding of the most effective ion pairs, which is a good application of SHAB principle.

   The comparison between hard and soft acids and between hard and soft bases is given in Tables 1.18 and 1.19, respectively.

Table 1.18 Comparison between hard and soft acids

Hard acids	Soft acids
i. Small size	i. Large size
ii. Absence of any outer electron which is easily excited to higher states	ii. Several easily excitable valence electrons
iii. High positive oxidation state	iii. Zero or low positive oxidation state
iv. Low polarisability	iv. High polarisability
v. High electronegativity	v. Low electronegativity
vi. $H^{\oplus}$, $Li^{\oplus}$, $Na^{\oplus}$, $K^{\oplus}$	vi. $Cu^{\oplus}$, $Ag^{\oplus}$, $Hg^{\oplus}$
vii. Al^{3+}, Fe^{3+}, Co^{3+}, Cr^{3+}	vii. $I^{\oplus}$, I_2, Br_2, $Br^{\oplus}$
viii. Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}	viii. Cd^{2+}, Pt^{2+}, Hg^{2+}, Pt^{4+}
ix. CO_2, SO_3	ix. Cl, Br, I, N
HX (hydrogen-bonding molecules)	M° (metal atoms) and bulk metals

Table 1.19 Comparison between hard and soft bases

Hard bases	Soft bases
i. High electronegativity	i. Low electronegativity
ii. Presence of filled orbitals	ii. Partially filled orbitals
iii. Low polarisability	iii. High polarisability
iv. Empty orbitals may exist at high energy level	iv. Empty orbitals are low lying
$CH_3CO_2^{\ominus}$, PO_4^{3-}, SO_4^{2-}	$SCN^{\ominus}$, $CN^{\ominus}$, $S_2O_3^{2-}$
H_2O, $\overset{\ominus}{O}H$, $F^{\ominus}$, $Cl^{\ominus}$	$H^{\ominus}$, $I^{\ominus}$
NH_3, N_2H_4, RNH_2	R_3P, R_3As
NO_3, CO_3^{2-}, $ClO_4^{\ominus}$	R_2S, RSH, $RS^{\ominus}$

Levelling solvents: Whenever an acid is dissolved in water, it acts as an acid only if the solvent acts as a base. That is, if we dissolve acids such as HCl, HNO_3, etc. in water, their acidic strength is almost the same, since water acts as a base for both these acids. In fact, it is known that all strong acids show equal acidic strength when dissolved in water. This is because water acts as a base to all these acids and thus forces them to donate almost the same amount of protons irrespective of their chemical nature. Since water levels the acidic strength of strong acids, it is referred to as a levelling solvent. In order to measure the strength of strong acids, they are dissolved in glacial acetic acid and the amount of protons is measured by conductometry. It is found that the strength of acids varies as

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$$

Amphiprotic species: Many molecules and ions can behave like water and may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic, e.g.

Acid$_1$		Base$_2$		Acid$_2$		Base$_1$
HBr	+	$HS^{\ominus}$	$\rightleftharpoons$	H_2S	+	$Br^{\ominus}$
$HS^{\ominus}$	+	$\overset{\ominus}{O}H$	$\rightleftharpoons$	H_2O	+	S^{2-}
$H_3O^{\oplus}$	+	$HCO_3^{\ominus}$	$\rightleftharpoons$	H_2CO_3	+	H_2O
$HCO_3^{\ominus}$	+	$CN^{\ominus}$	$\rightleftharpoons$	HCN	+	CO_3^{2-}

1.41 USANOVICH CONCEPT OF ACIDS AND BASES

According to Usanovich an acid is a chemical species which reacts with bases, gives up cations or accepts anions or electrons, and conversely a base is any chemical species which reacts with acids, gives up anions or combines with cation. For example,

$$SO_2 + Na_2O \longrightarrow Na_2SO_3$$
$$Cl_2 + 2Na \longrightarrow 2NaCl$$
$$Fe(CN)_2 + 4NaCN \longrightarrow Na_4[Fe(CN)_6]$$

We will discuss Hydrogen Bonding; Geometry, Shape, Hybridisation and Dipole Moment of Compounds and Ions; and Lanthanides and Actinides Contraction in Chapter 2.

ILLUSTRATION 1.81

Arrange the order of decreasing/increasing properties given below:

1. **Decreasing order of atomic and ionic radii**
   a. $Mg^{2+}, O^{2-}, Na^{\oplus}, F^{\ominus}$
   b. $Cl^{\ominus}, S^{2-}, Ca^{2+}$, Ar
   c. $N^{3-}, Na^{\oplus}, F^{\ominus}, O^{2-}, Mg^{2+}$
   d. S, O, Se, C
   e. B, Be, Li, Na
   f. $Li^{\oplus}, Na^{\oplus}, K^{\oplus}, Rb^{\oplus}, Cs^{\oplus}$ (in aqueous solution)
   g. $Cl^{7+}, Si^{4+}, Mg^{2+}, Na^{\oplus}$
   h. $H^{\oplus}$, Li, $H^{\ominus}$
   i. $O^{2-}, B^{3+}, Li^{\oplus}, F^{\ominus}$
   j. $Br^{\ominus}$, I, $I^{\ominus}$, $I^{\oplus}$
   k. $I^{\ominus}$, I, $I^{\oplus}$
   l. $K^{\oplus}, Ca^{2+}, Ti^{3+}, Ti^{4+}$
   m. Ce, Sn, Yb, Lu
   n. F, $F^{\ominus}$, O, O^{2-}
   o. Ar, Br, Ca^{2+}, Mg^{2+}
2. **Decreasing order of IE**
   a. Mg, Al, Si, Na
   b. Decreasing IE_1 of the following:
      Ar, Cl, P, S, Si, Mg, Al, Na
   c. Decreasing IE_2 of the following:
      Na, Ar, Cl, S, P, Al. Si, Mg
   d. IE of completely filled, half filled and incompletely filled orbitals.
   e. N, O, F
   f. B, C, N, O
   g. F, Cl, Br, I
   h. Ne, O, Na, $Na^{\oplus}$
   i. Cu, Ag, Au
   j. Na, K, Mg, Kr
   k. F, Cl, O, N
   l. Li, Na, K
   m. Be, Mg, Ca
   n. B, C, N
   o. Ge, Si, C
   p. Ti, V, Cr, Mn
   q. B, Al, Ga, In, Tl
   r. IE_2 of 2nd period elements
3. **Decreasing order of $\Delta_{eg}H^{\ominus}$**
   a. F, Cl, Br, I
   b. N and P
   c. B, Al
   d. O, S
   e. O, N, F, S
   f. B, C, N, O
   g. Cl, F, Br, I, S, Si
   h. $S^{\ominus}$, O
   i. $N^{\ominus}$, P
   j. S, $O^{\ominus}$
   k. $O^{\ominus}, S^{\ominus}$
   l. O, $O^{\oplus}$, O^{2+}, O^{2-}
   m. Li, Be, Na, Ne
   n. C, N, Be, F, O Cl
4. **Decreasing order of EN**
   a. As, P, S, Cl
   b. $O^{\oplus}$, O, $O^{\ominus}$

c. H, O, Al, F
d. F, N, O, Cl, S
e. $M^{\oplus}$, M^{2+}, M^{3+}, M^{4+}
f. F, Cl, Br, I
g. N, P, C, Si
h. P, S, N, O
i. Zn, Cd, Hg
j. H, P, S, Te
k. $X^{\ominus}$, X, X^{2-}
l. Decreasing order of EN of carbon in the following: CH_4, $CH_2=CH_2$, $HC\equiv CH$
m. Decreasing order of EN of Cl atom in, Cl_2O_7, Cl_2O_5, ClO_2, ClO

5. **Decreasing order of acidic property/strength**
a. ZnO, Na_2O_2, P_2O_5, MgO
b. CO_2, N_2O_5, SiO_2, SO_3
c. HClO, $HClO_2$, $HClO_3$, $HClO_4$
d. HNO_3, H_3PO_4, H_3AsO_4, H_3SbO_4
e. H_2O, H_2S, H_2Te, H_2Se
f. H_2SO_3, H_2SeO_3, H_2TeO_3
g. SO_4, H_2SeO_4, H_2TeO_4
h. HF, HCl, HBr, HI
i. HOCl, HOBr, HOI
j. Al_2O_3, MgO, SiO_2, P_4O_{10}
k. Increasing pH of aqueous solution of LiCl, $BeCl_2$, $MgCl_2$, $AlCl_3$

6. **Decreasing order of basic property/strength**
a. MgO, SrO, K_2O, NiO, Cs_2O
b. LiOH, NaOH, KOH, RbOH, CsOH
c. $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$
d. NH_3, AsH_3, SbH_3, PH_3
e. Li_2O, BeO, B_2O_3, CO_2
f. $F^{\ominus}$, $Cl^{\ominus}$, $Br^{\ominus}$, $I^{\ominus}$
g. $F^{\ominus}$, $\overset{\ominus}{O}H$, $\overset{\ominus}{N}H_2$, $\overset{\ominus}{C}H_3$
h. Al_2O_3, Tl_2O_3, Tl_2O, Ga_2O_3

7. **Decreasing order of ionic character**
a. $CaCl_2$, $BeCl_2$, $MgCl_2$, $BaCl_2$, $SrCl_2$
b. BCl_3, $AlCl_3$, $GaCl_3$
c. VCl_2, VCl_3, VCl_4, $VOCl_3$
d. LiBr, NaBr, KBr, RbBr, CsBr
e. LiF, K_2O, ClF_3, SO_3, N_2
f. P_2O_5, CrO_3, MnO, Mn_2O_7

8. **Decreasing order of covalent character**
a. LiCl, LiBr, LiI
b. $TiCl_2$, $TiCl_3$, $TiCl_4$
c. NaCl, $MgCl_2$, $AlCl_3$, $SiCl_4$, PCl_5, SF_6, IF_7
d. CCl_4, $SiCl_4$, $GeCl_4$, $SnCl_4$, $PbCl_4$
e. CCl_4, CBr_4, CI_4
f. $LaCl_3$, $CeCl_3$, $GdCl_3$, $LuCl_3$

9. **Decreasing order of melting and boiling points**
a. Melting points of Li, Na, K, Rb, Cs
b. Melting and boiling points of hydrides of group 15
c. Melting and boiling points of hydrides of group 16
d. Melting and boiling points of hydrides of group 17
e. Melting and boiling points of H_2O, HF and NH_3
f. Melting points of KCl, KBr, KF, KI
g. Melting points of CaF_2, $CaCl_2$, $CaBr_2$, CaI_2
h. Melting points of LiBr, $BeBr_2$, BBr_3, LiI

10. **Decreasing order of magnetic moment and also mention whether they are coloured or colourless**
a. Ti^{3+}, Ni^{2+}, Cr^{2+}, Co^{2+}, Zn^{2+}
b. Ca, A, N, O
c. Sc, Ti, V, Cr, Mn, Fe
d. $Sc^{\oplus}$, $Ti^{\oplus}$, $V^{\oplus}$, $Cr^{\oplus}$, $Mn^{\oplus}$, $Fe^{\oplus}$
e. Sc^{2+}, Ti^{2+}, V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}
f. Sc^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}
g. Al, Si, P, S, Cl

11. **Decreasing order of bond angles**
a. NH_3, PH_3, AsH_3
b. H_2O, H_2S, H_2Se
c. NF_3, PH_3, AsF_3
d. NF_3, NCl_3
e. $NO_2^{\oplus}$, NO_2, $NO_2^{\ominus}$
f. NH_3, NF_3
g. PH_3, PF_3
h. CH_4, NH_3, H_2O, BF_3, C_2H_2
i. H_2O, CO_2, NH_3, CH_4
j. NH_3, $\overset{\oplus}{N}H_4$, PCl_5, SCl_2
k. $NO_3^{\ominus}$, $NO_2^{\ominus}$, $NO_2^{\oplus}$, NO_2
l. BF_3, NH_3, SiH_4, H_2S
m. Cl_2O, ClO_2, Cl_2O_7, $I_3^{\ominus}$

12. **Decreasing order of solubility**
a. BeF_2, MgF_2, CaF_2, BaF_2
b. $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$
c. $BeCO_3$, $MgCO_3$, $CaCO_3$, $BaCO_3$
d. $BeSO_4$, $MgSO_4$, $CaSO_4$, $BaSO_4$
e. $Be(HCO_3)_2$, $Mg(HCO_3)_2$, $Ca(HCO_3)_2$, $Ba(HCO_3)_2$
f. NaCl, $MgCl_2$, $AlCl_3$, CCl_4
g. NaCl, CuCl (note the size of $Na^{\oplus}$ = size of $Cu^{\oplus}$)
h. HNO_3, H_3PO_4, H_3AsO_4, H_3SbO_4
i. H_2SO_3, H_2SeO_3, H_2TeO_3

13. Decreasing order of bond strength or bond dissociation enthalpy and bond length

a. Bond length and bond strength of F_2, N_2, Cl_2, O_2

b. Single bond strength: N_2, O_2, F_2

c. Bond dissociation enthalpy: F_2, Cl_2, Br_2, I_2

d. Bond strength and thermal stability: HCl, HBr, HF, HI

e. Thermal stability: HClO, $HClO_2$, $HClO_3$, $HClO_4$

f. Thermal stability: LiOH, NaOH, KOH, RbOH CsOH

g. Thermal stability and reducing character: NH_3, AsH_3, SbH_3, PH_3

h. Thermal stability and reducing character: H_2O, H_2S, H_2Se, H_2Te

i. Thermal stability: H_2SO_3, H_2SeO_3, H_2TeO_3

j. Thermal stability: H_2SO_4, H_2SeO_4, H_2TeO_4

k. Thermal stability: HFO_3, $HClO_3$, $HBrO_3$, HIO_3

l. Thermal stability: LiH, NaH, KH, CsH

m. Thermal stability: $BeCO_3$, $MgCO_3$, $CaCO_3$, $BaCO_3$

n. Stability: $Li^{\ominus}$, $Be^{\ominus}$, $B^{\ominus}$, $C^{\ominus}$

14. Decreasing order of extent of hydrolysis, hydration of ions and hydration energy

a. **Extent of hydrolysis:** CCl_4, $MgCl_2$, $AlCl_3$, PCl_5, $SiCl_4$

b. **Extent of hydrolysis:** NCl_3, PCl_3, $AsCl_3$, $SbCl_3$, $BiCl_3$

c. **Hydration of ions:** Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}

d. **Hydration energy:** $Li^{\oplus}$, $Na^{\oplus}$, $K^{\oplus}$, $Rb^{\oplus}$, $Cs^{\oplus}$

e. **Hydration energy:** $K^{\oplus}$, $Cs^{\oplus}$, Ca^{2+}, Ba^{2+}

15. Decreasing order of strength of Lewis acids

a. BF_3, BCl_3, BBr_3

b. $AlCl_3$, $GaCl_3$, $InCl_3$

16. Decreasing order of oxidising/reducing power

Decreasing oxidising power:

a. $GeCl_4$, $SnCl_4$, $PbCl_4$

b. F, Cl, Br, I

c. O, S, Se, Te

d. $BrO_4^{\ominus}$, $ClO_4^{\ominus}$, $IO_4^{\ominus}$

e. $ClO^{\ominus}$, $BrO^{\ominus}$, $IO^{\ominus}$

Decreasing reducing power:

f. $GeCl_2$, $SnCl_2$, $PbCl_2$

g. HF, HCl, HBr, HI

17. Decreasing order of miscellaneous properties as indicated.

a. **Decreasing strength of hydrogen bonding (X .... H–X)** O, S, F, Cl, N

Decreasing reactivity with water:

b. Li, Na, K, Rb, Cs

c. Be, Mg, Ca, Sr, Ba

d. Decreasing reactivity with hydrogen: Li, Na, K, Rb, Cs

e. Decreasing reactivity towards air: Be, Mg, Ca, Sr, Ba

f. Decreasing number of hybrid orbitals: C, Si, Sn

g. Decreasing oxidation number of iodine: I_2, HI, HIO_4, ICl

h. Decreasing order of +5 oxidation state: N, P, As, Sb, Bi

i. Decreasing poisonous nature: H_2O, H_2S, H_2Se, H_2Te, H_2Po

j. Decreasing affinity for hydrogen: F_2, Cl_2, Br_2, I_2

k. Decreasing electropositivity: Fe, N, Cu, Li

l. Decreasing density: Fe, Pb, Al, Au

m. Decreasing density: H_2S, O_2, CO_2, NH_3, H_2

Sol.

1. a. $O^{-2} > F^{\ominus} > Na^{\oplus} > Mg^{2+}$

Z	O = 8	F = 9	Na = 11	Mg = 12	(All species are iso-electronic)
e^-	8 + 2 = 10	9 + 1 = 10	11 − 1 = 10	12 − 2 = 10	
$\frac{Z}{e}$	$\frac{8}{10}$ = 0.8	$\frac{9}{10}$ = 0.9	$\frac{11}{10}$ = 1.1	$\frac{12}{10}$ = 1.2	

Smaller the value of $\frac{Z}{e}$, larger is the size.

Hence the order is as given above.

b. $\underbrace{S^{2-} > Cl^{\ominus} > Ar >}_{\text{All belong to 3rd period}} \underbrace{Ca^{2+}}_{\text{4th period}}$ (All speices are isoelectronic)

i. Size of element decreases along the same period (→) but the size of noble gas is maximum in that period (due to greater electron–electron repulsion).

ii. Size of Ca (4th period) > size of Ar (3rd period), but the size of Ar > size of Ca^{2+}. Therefore,

Size of dinegative ion > size of mononegative ion > noble gas (of the same period) > size of dipositive cation.

Hence the order is as given above.

c. $N^{3-} > O^{2-} > F^{\ominus} > Na^{\oplus} > Mg^{2+}$ (All species are isoelectronic)

Z	N = 7	O = 8	F = 9	Na = 11	Mg = 12
e^-	7 + 3 = 10	8 + 2 = 10	9 + 1 = 10	11 − 1 = 10	12 − 2 = 10

Same explanation as in parts (a) and (b) above

d. $\underset{\text{4th Period}}{\text{Se}} > \underset{\text{3rd Period}}{\text{S}} > \underset{\text{2nd Period}}{\text{C}} > \underset{\text{2nd Period}}{\text{O}}$

Size of atom increases down the group because of addition of new shell (or increase in principal quantum number n).

Size of atom decreases along the period (→), i.e. decreases from C to O.

e. $\underset{\text{3rd Period}}{Na} > \underset{\text{2nd Period}}{Li} > \underset{\text{2nd Period}}{Be > B}$

Same explanation as in part (d) above.

f. $Li^{\oplus} > Na^{\oplus} > K^{\oplus} > Rb^{\oplus} > Cs^{\oplus}$ (in aqueous solution)

The ions in solution are present as hydrated ions. The smaller the size of the ion, greater is the charge density and hence greater is the extent of hydration. So, the size of hydrated ions becomes larger for the smaller sized ion and vice versa.

g. $Na^{\oplus} > Mg^{2+} > Si^{4+} > Cl^{7+}$ (All species are isoelectronic)

Z	Na = 11	Mg = 12	Si = 14	Cl = 17
$\bar{e}$	11 − 1 = 10	12 − 2 = 10	14 − 4 = 10	17 − 7 = 10

Smaller the charge on the cation, larger is the size and vice versa.

h. $H^{\ominus} > Li > H^{\oplus}$ (The species are not isoelectronic)

Z	H = 1	Li = 3	H = 1
$\bar{e}$	1 + 1 = 2	3 + 0 = 3	1 − 1 = 0
$\frac{Z}{\bar{e}}$	$\frac{1}{2} = 0.5$	$\frac{3}{8} = 1.0$	—

Smaller the value of $\frac{Z}{e^-}$, larger is the size.

i. $O^{2-} > F^{\ominus} > Li^{\oplus} > B^{3+}$ (All species are not isoelectronic, but all of them belong to the same 2nd period)

Z	O = 8	F = 9	Li = 3	B = 5
$\bar{e}$	8 + 2 = 10	9 + 1 = 10	3 − 1 = 2	5 − 3 = 2

Higher the –ve charge, larger is the size and higher the +ve charge, smaller is the size of an ion.

j. $\underbrace{I^{\ominus} > I^{\ominus} > I^{\oplus}}_{\text{5th period}} > \underbrace{Br^{\oplus}}_{\text{4th period}}$ [All the species are not-isoelectronic]

Z	I = 53	I = 53	I = 53	Br = 35
e^-	53 + 1 = 54	53 + 0 = 53	53 − 1 = 52	35 + 1 = 36

Same explanation as in (a) and (b) above.

k. $I^{\ominus} > I > I^{\oplus}$ [Same explanation as in (j)]

l. $K^{\oplus} > Ca^{2+} > Ti^{3+} > Ti^{4+}$ [Same explanation as in (g)]

m. (Z for Ce = 58, Sn = 60, Yb = 70 and Lu = 71)

$\underbrace{Sn}_{\text{5th Period}} > \underbrace{Yb > Ce > Lu}_{\text{6th Period Lanthanides}}$

In lanthanides, the size decreases from La to Lu (Z = 57 to 71) due to lanthanide contraction. Although Sn belongs to the 5th period but its size is larger than lanthanides.

n. $O^{2-} > F^{\ominus} > O > F$

(The species are not isoelectronic)

[Same explanation as in parts (a) and (d) above]

o. $Br > Ar > Ca^{2+} > Mg^{2+}$

[Refer to solved example 1.5 (b)]

2. a. Si > Mg > Al > Na

(All of them belong to the same 3rd period)

IE (kJ mol^{-1}) 1577 > 737 > 577 > 496

IE increases along the period (→)

But there is an exception, IE_1 of Mg > IE_1 of Al.

This is due to penetration effect.

The valence electronic configurations of Mg and Al are

$Mg = 3s^2$, $Al = 3s^2\,3p^1$

It is easier to remove electron from 3p orbital than 2s orbital, since 2s is more penetrated towards nucleus. Hence the order is as given above.

b. $\underbrace{Ar > Cl > \boxed{P > S} > Si > \boxed{Mg > Al} > Na}_{\text{All of them belongs to 3rd period}}$

3rd period element

Group	1	2	—	13	14	15	16	17	18
Element	Na	Mg		Al	Si	P	S	Cl	Ar

Generally IE_1 increasing along the period.

With an exception, IE_1 of Mg > IE_1 of Al (due to penetration effect).

Similarly, there is an exception, IE_1 of P > IE_1 of S [due to stable half filled orbitals in P]

c. **IE_2:** All of these elements belong to 3rd period

$\boxed{Na > Ar} > Cl > Si > P > \boxed{Al > Si} > Mg$

Generally IE_2 also increases along the period, but there are two exceptions as marked in the box.

1st exception: IE_2 of Na > IE_2 of Ar

Electronic configuration:

Na (Z = 11), $1s^2\,2s^2\,2p^6\,3s^1$, $Na^{\oplus}$ = ... $3s^0$, Na^{2+} = ... $2s^2 2p^5$

IE_1 of Na is very low. IE_2 is the highest among the given elements, since it is very difficult to remove electron from inner (2p) orbitals.

Ar (Z = 18): $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$, $Ar^{\oplus}$ = ... $3s^2 3p^5$; Ar^{2+} =..... $3s^2 3p^4$

IE_1 of Ar is very high since it is very difficult to remove electron from stable full-filled configuration ($3s^2 3p^6$). But IE_2 of Ar is less than IE_2 of Na, since in case of Na, electron has to be removed from the inner 2p orbital, whereas in the case of Ar, it has to be removed from the valence 3p orbital.

Alternatively: Larger the value of $\frac{Z}{e^-}$, smaller is the size and high is the IE and vice versa.

Na ($Z = 11$), $Na^{\oplus}$ ($11 - 1 = 10$), $\frac{Z}{e} = \frac{11}{10} = 1.1$,

Na^{2+} ($11 - 2 = 9$), $\frac{Z}{e^-} = \frac{11}{9} = 1.22$

Ar ($Z = 18$), $Ar^{\oplus}$ ($18 - 1 = 17$), $\frac{Z}{e} = \frac{18}{17} = 1.05$,

Ar^{2+} ($18 - 2 = 16$), $\frac{Z}{e} = \frac{18}{16} = 1.125$

$\therefore \frac{Z}{e^-}$ for both $Na^{\oplus}$ and Na^{2+} > $\frac{Z}{e^-}$ for both $Ar^{\oplus}$ and Ar^{2+}

Hence IE_2 of Na > IE_2 of Ar

IE_2 of Cl	>	IE_2 of S
(2298)		(2252) kJ mol^{-1}

Note: From the electronic configuration and $\frac{Z}{e}$ value, IE_2 of S should be > IE_2 of Cl, but the observed values are reversed.

Therefore, this discrepancy has to be explained by calculating Z_{eff} (effective nuclear charge) using Slater rule. Higher the Z_{eff}, higher is the IE_2.

i. **Z_{eff} for last electron in $Cl^{\oplus}$:**

Electron configuration of Cl and $Cl^{\oplus}$

Cl ($Z = 17$) = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

$$Cl^{\oplus} = \underbrace{1s^2}_{2\bar{e}},\ \underbrace{2s^2\ 2p^6}_{8\bar{e}}\ \underbrace{3s^2\ 3p^4}_{2+3=5\bar{e}}$$

$\therefore$ σ for last electron in $Cl^{\oplus}$

$$= \begin{bmatrix} 0.35 \times \text{No. of electrons left in the } n\text{th shell} \\ + (0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) \\ + (1.00 \times \text{Total no. of electrons in the inner shells}) \end{bmatrix}$$

$= 0.35 \times 5 + 0.85 \times 8 + 1.00 \times 2 = 10.55$

Z_{eff} for $Cl^{\oplus} = Z - \sigma = 17 - 10.55 = 6.45$

ii. **Z_{eff} for last electron in $S^{\oplus}$:**

Electron configuration of S and $S^{\oplus}$

S ($Z = 16$) = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

$$S^{\oplus} = \underbrace{1s^2}_{2e^-}\ \underbrace{1s^2\ 2p^6}_{8e^-}\ \underbrace{3s^2\ 3p^3}_{2+2=4e^-}$$

$\therefore$ σ for last electron in $S^{\oplus}$

$= (0.35 \times 4 + 8 \times 0.85 + 1.00 \times 2) = 10.2$

Z_{eff} for $S^{\oplus} = Z - \sigma = 16 - 10.2 = 5.8$

$\therefore Z_{eff}$ for $Cl^{\oplus} > Z_{eff}$ for $S^{\oplus}$

Hence IE_2 of Cl > IE_2 of S

2nd exception: IE_2 of Al > IE_2 of Si

Electronic configuration:

Al ($Z = 13$), $1s^2$, $2s^2\ 2p^6$, $3s^2\ 3p^1$

$Al^{\oplus}$ = ... $3s^2\ 3p^0$, Al^{+2} = ... $3s^1$

Si($Z = 14$), $1s^2$, $2s^2\ 2p^6$, $3s^2\ 3p^2$

$Si^{\oplus}$ = ... $3s^2\ 3p^1$, Si^{+2} = ... $3s^2 3p^0$

IE_2 of Al > IE_2 of Si, since in case of Al, the second electron has to be removed from 3*s* orbital (which is more penetrated toward nucleus) whereas in case of Si, the second electron has to be removed from 3*p* orbital (which is less penetrated than *s*-orbital) (Penetration effect). Hence IE_2 of Al > IE_2 of Si.

Alternatively: Larger the value of $\frac{Z}{e^-}$, smaller is the size and high is the IE_2 and vice versa.

d. IE of completely filled > half filled > incompletely filled orbitals.

Since completely filled orbitals are more stable (due to high release of exchange energy) than half-filled orbitals which in turn more stable than incompletely filled orbitals.

Al ($Z = 13$), $Al^{\oplus}$($13 - 1 = 12$), $\frac{Z}{e} = \frac{13}{12} = 1.083$

Al^{2+} ($13 - 2 = 11$), $\frac{Z}{e} = \frac{13}{11} = 1.18$

Si ($Z = 14$), $Si^{\oplus}$ ($14 - 1 = 13$), $\frac{Z}{e} = \frac{14}{13} = 1.076$

Si^{2+} ($14 - 2 = 12$), $\frac{Z}{e} = \frac{14}{12} = 1.166$

$\therefore \frac{Z}{e}$ for both $Al^{\oplus}$ and Al^{2+} > $\frac{Z}{e}$ for both $Si^{\oplus}$ and Si^{2+}

Hence IE_2 of Al > IE_2 of Si

e. F > $\boxed{N > O}$

IE increases along the period (→).

But there is exception, IE_1 of N > IE_1 of O.

This is due to half-filled stable configuration in N.

f. N > O > C > B (same explanation as in part (b) above)

g. F > Cl > Br > I (generally IE decreases down the group (↓))

h. $\frac{\text{Ne}}{\text{2nd period}} > \frac{Na^{\oplus}}{\text{3rd period}} > \frac{\text{O}}{\text{2nd period}} > \frac{\text{Na}}{\text{3rd period}}$

For explanation refer to solved example 1.5 (f).

i. Cu > $\boxed{Ag < Au}$ (Cu, Ag and Au belongs to 3*d*, 4*d* and 5*d* transition element series).

Generally IE decreases from Cu →Ag →Au. But there is an exception, IE_1 of Au > IE_1 of Ag.

Explanation: In all the 3 cases an *s*-electron in the unpaired state is to be removed. In the case of Cu a 4*s* electron is to be removed which is closer to the nucleus than the 5*s* electron of Ag. So IE decreases from Cu to Ag. However from Ag to Au, the 14*f*-electrons are added which provide very poor shielding effect. The nuclear charge is thus enhanced and therefore the outer electron of Au is more tightly held and so the IE_1 of Au is high.

j.

Element	Kr >	Mg >	Na >	K
IE_1 (kJ mol^{-1})	1351 >	737 >	496	419
Group	18	2	1	1

Generally IE decreases down the group (↓) and IE_1 of group 2 > IE_1 of group 1.

Kr being inert gas has the maximum IE_1 as the process involves removal of electron from the stable $4s^2\,4p^6$ configuration.

k.

Elements	F >	N >	O >	Cl
IE_1 (kJ mol^{-1})	1680 >	1402 >	1314 >	1256
Period	2	2	2	3

IE_1 of 2nd period > IE_1 of 3rd period. So IE_1 of Cl is the least [i.e. IE decreases down the group (↓)]

IE_1 increases along the period, so IE_1 of F is the highest.

There is an exception; IE_1 of N > IE_1 of O.

This is due to the stable half-filled orbitals in N.

l. Li > Na > K [All of them belong to group 1 and IE decreases down the group (↓)]

m. Be > Mg > Ca [All of them belong to group 2 and IE decreases down the group (↓)]

n. N > C > B [All of them belong to 2nd period and IE increases along the period (→)]

o. C > Si > Ge [All of them belong to group 14 and IE decreases down the group (↓)]

p.

Element	Mn >	Cr >	V >	Ti
Z	25	24	23	22
IE_1 (kJ mol^{-1})	717 >	653 >	650 >	646

[All of them belong to 3*d* transition element series and IE increases along the period]

q. IE_1 should be B > Al > Ga > In > Tl (IE_1 decreases down the group).

But the observed order is

IE_1	B >	Tl >	Ga >	Al >	In
(kJ mol^{-1})	800 >	590 >	579 >	577 >	558

Note: There is a deviation from general trend.

This is due to the inert pair effect and which is due to the imperfect (or poor) screening effect of *d*- and *f*-electrons.

i. In Ga, due to the poor screening effect of 3*d* electrons, size of $Ga^{\oplus}$ < size of $Al^{\oplus}$, so the IE_1 of Ga > IE_1 of Al.

ii. In Tl, due to poor screening effect of 4*f*- electrons (screening effect of $s > p > d > f$ orbitals).

∴ IE_1 of Tl > Ga > Al > In

Hence the order is as given above.

r. 2nd period elements from left to right are

Li, Be, B, C, N, O, F, Ne

The electronic configuration of these elements and their ions in +1 oxidation states are as

i. Li (Z = 3), → $2s^1$, $Li^{\oplus} \Rightarrow 2s^0$ [stable noble gas configuration and IE_2 is the highest in 2nd period]

ii. Be (Z = 4) ⇒ $2s^2$, $Be^{\oplus} \Rightarrow 2s^1$, $Be^{2+} \Rightarrow 2s^0$.

[Most stable]

Therefore, IE_2 of Be is lower than of B.

iii. B (Z = 5), ⇒ $2s^2\,2p^1$, $B^{\oplus} \Rightarrow 2s^2\,2p^0$

[Stable noble gas configuration]

∴ IE_2 of B > Be

iv. C (Z = 6) ⇒ $2s^2\,2p^2$, $C^{\oplus} \Rightarrow 2s^2\,2p^1$

Due to penetration effect, i.e. it is easier to remove an 2*p* electron from $C^{\oplus}$ than from 2*s* electron from $B^{\oplus}$

∴ IE_2 of B > C

v. From C to N to O, nuclear charge increases by one unit at a time. Therefore, their IE_2 also increases accordingly, i.e. IE_2 of O > N > C

vi. O (Z = 8) ⇒ $2s^2 2p^4$, $O^{\oplus} \Rightarrow 2s^2\,2p^3$

[Half-filled stable configuration]

vii. F (Z = 9) ⇒ $2s^2 2p^5$, $F^{\oplus} = 2s^2 2p^4$

∴ IE_2 of O > F

viii. Ne (Z = 10) ⇒ $2s^2 2p^6$, $Ne^{\oplus} \Rightarrow 2s^2 2p^5$

Since Ne, has the highest nuclear charge in 2nd period, therefore IE_2 of Ne is expected to be much higher than that of O and F,

∴ IE_2 of Ne > O > F

Hence decreasing order of IE_2 of 2nd period is

Li > Ne > O > F > N > B > C > Be

3. a. $\boxed{Cl > F}$ > Br > I

[$\Delta_{eg}H^{\ominus}$ decreases down group (↓) but there is an exception in $\Delta_{eg}H^{\ominus}$ of Cl and F]

$\Delta_{eg}H^{\ominus}$ of Cl > $\Delta_{eg}H^{\ominus}$ of F.

It is due to very small size of F atom. There are strong electron–electron repulsion in the relatively small 2*p* orbitals of F and thus, the incoming electron does not experience much attraction. Hence, the incoming electron is not added easily as it is added in large 3*p* orbitals of Cl. Consequently, $\Delta_{eg}H^{\ominus}$ of F is less negative than that of Cl.

b. N = $2s^2\,2p^3$, P = $3s^2\,3p^3$

$\Delta_{eg}H^{\ominus}$ of P (more –ve value, –74 kJ mol^{-1}) > N (+ 20.1 kJ mol^{-1}). In both N and P, 2*p* and 3*p* orbitals are half-filled respectively. Thus the addition of extra

electron to these orbitals is not possible. But an extra electron is added much more easily in $3p$ orbitals of P than that of $2p$ orbital of N.

Consequently, $\Delta_{eg}H^{\ominus}$ of P is more negative than that of N.

c. $\Delta_{eg}H^{\ominus}$ of Al (more – ve, – 44 kJ mol^{-1}) > B (less – ve, –23 kJ mol^{-1}).

Note: $\Delta_{eg}H^{\ominus}$ of 2nd period have negative value than the corresponding of 3rd period.

Valence shell configuration of B and Al is as

$B = 2s^1 2p^1$, $\quad Al = 3s^2 3p^1$

Same explanation as in part (b) above.

d. $\Delta_{eg}H^{\ominus}$ of S (–200 kJ mol^{-1}) > O (–141 kJ mol^{-1})

Valence shell electronic configuration of O and S is as:

$O = 2s^2 2p^4$, $\quad S = 3s^2 3p^4$

Same explanation as in part (b) above.

e. N > O > S > F (from +ve value to increasing –ve values). (Refer to Illustration 1.43.)

f. N > B > C > O (from +ve value to increasing –ve values) (Refer to Illustration 1.45).

g. Cl > F > Br > I > S > Si

For explanation of $\Delta_{eg}H^{\ominus}$ of Cl > F > Br > I, [Refer to part (a) above.]

$\Delta_{eg}H^{\ominus}$ of $\underbrace{\underset{\text{gp 16}}{S} > \underset{\text{gp 14}}{Si}}_{\text{Both are of 3rd period}}$ (Generally $\Delta_{eg}H^{\ominus}$ increases along the period)

Hence the order is as given above.

For part (h) to (k), refer to Illustration 1.44.

h. $S^{\ominus} > O$ $\quad$ i. $N^{\ominus} > P$

j. $O^{\ominus} > S$ $\quad$ k. $O^{\ominus} > S^{\ominus}$

l. $O^{+2} > O^{\oplus} > O > O^{2-}$ (Greater the +ve charge, greater is the tendency to attract electron)

m. $\frac{Ne}{\text{gp 18}} > \frac{Be}{\text{gp 2}} > \frac{Li > Na}{\text{gp 1}}$ (Ne, Be and Li belong to the same 2nd period and Na belongs to the 3rd period)

$\Delta_{eg}H^{\ominus}$ of inert gases is the highest because of the stable completely filled ($2s^2\,2p^6$) configuration. So, energy is required to add extra electron.

$\Delta_{eg}H^{\ominus}$ of Be is comparable with Ne, because of the stable completely filled ($2s^2$) configuration.

Down the group (↓), $\Delta_{eg}H^{\ominus}$ decreases, so $\Delta_{eg}H^{\ominus}$ of Li > $\Delta_{eg}H^{\ominus}$ of Na.

Hence the order is as given above.

n. Cl > F > O > C > N > Be [refer to solved example 1.5(c)]

4.

a. $\underbrace{Cl > S > P}_{\text{All belong to the 3rd period}} > \underbrace{As}_{\text{4th period}}$

EN increases along the period (→) and decreases down the group (↓).

b. $O^{\oplus} > O > O^{\ominus}$

The positive charge on the atoms increases its EN while negative charge decreases its EN.

c. F > O > Al > H [refer to solved example 1.5(a)]

d. F > O > Cl > S > N [refer to solved example 1.5(e)]

e. $M^{+4} > M^{+3} > M^{+2} > M^{\oplus}$ (As the polarising power increases, EN increases)

f. F > Cl > Br > I [EN decreases down the group (↓)]

g. $\underbrace{\underset{\text{gp 15}}{N} > \underset{\text{gp 14}}{C}}_{\text{2nd period}} > \underbrace{\underset{\text{gp 15}}{P} > \underset{\text{gp 15}}{Si}}_{\text{3rd period}}$ [EN increases along the period (→) and decreases down the group (↓)]

h. $\underbrace{\underset{\text{gp 16}}{O} > \underset{\text{gp 15}}{N}}_{\text{2nd period}} > \underbrace{\underset{\text{gp 16}}{S} > \underset{\text{gp 15}}{P}}_{\text{3rd period}}$ [EN of O, N, S and P are 3.5, 3, 2.5 and 2.1, respectively]

Same explanation as in part (g) above.

i. $\underbrace{\underset{3d}{Hg} > \underset{4d}{Cd} > \underset{5d}{Zn}}_{\text{Transition element series}}$ (They belong to group 12 or III B)

In case of Zn, Cd and Hg, EN increases down the group.

j. S > H = P = Te

Note: EN of H, P and Te are 2.1 each. EN of S = 2.6. It is an experimental fact.

k. $X > X^{\ominus} > X^{-2}$ [Higher the positive charge or lower the negative change, higher is the EN. Refer to Section 1.15.3, Point (4)]

l. $\underset{sp}{CH \equiv CH} > \underset{sp^2}{CH_2 = CH_2} > \underset{sp^3}{CH_4}$

[Refer to Section 1.15.3, Point (6)]

More the s-character in hybrid orbital, higher the EN.

m. EN of central atom ∝ 0.5

$\overset{+7}{Cl_2O_7} > \overset{+5}{Cl_2O_5} > \overset{+4}{ClO_2} > \overset{+2}{ClO}$

5.

a. $\underbrace{\overset{5+}{P_2O_5}}_{\text{Acidic}} > \underbrace{\overset{2+}{ZnO}}_{\text{Amphoteric}} > \underbrace{\overset{2+}{MgO}}_{\text{Less basic}} > \underbrace{\overset{1+}{Na_2O_2}}_{\text{More basic}}$

Acidic character of oxides increases along the period (→). According to Fajans' rule, higher the oxidation state of the atom, more is the covalent character and more is the acidic character.

In case of ZnO and MgO, both have +2 charge on the atom. But the size of Mg^{2+} > size of Zn^{2+}. The smaller the cation, the more covalent and more acidic the solution.

Zn belongs to $3d$ transition element series, so the size decreases along the $3d$ series (→).

Alternatively: Oxides of electropositive elements are alkaline while those of electronegative elements are acidic. Alkaline property will increase with the increase of electropositive character of metal and acidic characteristic

increase with the increase of electronegative characteristics of non-metals. Since the electronegativity decrease in the order P > Zn > Mg >Na the acidic character of oxide will also decrease in the same order.

b. $\overset{6+}{SO_3} > \overset{5+}{N_2O_5} > \overset{4+}{CO_2} > \overset{4+}{SiO_2}$

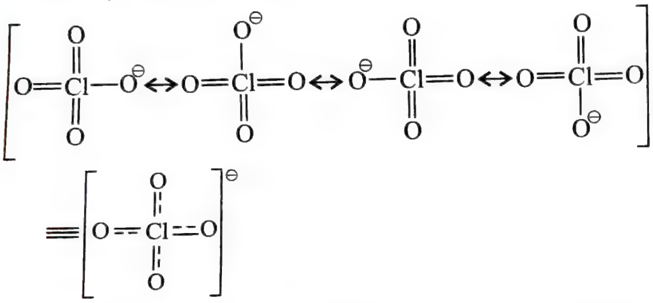
In case of CO_2 and SiO_2 both have +4 charge on the atom. But the size of Si^{4+} > size of C^{4+} (size increases down the group, and both belong to group 14).

Rest is same explanation as in part (a) above.

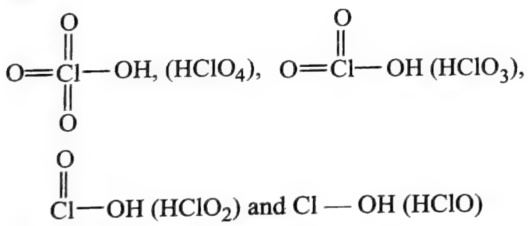
c. $HClO_4 > HClO_3 > HClO_2 > HClO$.

The more stronger the acid, the weaker will be its conjugate base. In $HClO_4$, $ClO_4^{\ominus}$ is the conjugate base and therefore it is stabilised by four resonating structure. Hence more acidic. Similarly, $ClO_3^{\ominus}$, $ClO_2^{\ominus}$ and $ClO^{\ominus}$ will have 3, 2 and 1 resonating structure. Hence the order is as given above. For example,

$HClO_4 + H_2O \longrightarrow H_3O^{\oplus} +$



Alternatively: These acids are oxoacids and are represented as



The larger number of O-atoms attached to Cl, the greater the pull towards O-atom, hence it is more easy to remove hydrogen from acid.

d. $\overset{5+}{HNO_3} > \overset{5+}{H_3PO_4} > \overset{5+}{H_3AsO_4} > \overset{5+}{H_3SbO_4}$ (All are oxo-acids)

All of them belong to group 15. Size of central atom increases down the group. According to Fajans' rule, smaller is the size of cation, more covalent character and thus more acidic. Hence the order is as given above.

e. $H_2Te > H_2Se > H_2S > H_2O$

Note: These are not oxoacids but are hydrides of group 16.

The acidic strength depends on M–H bonds. The larger the size of M (O, S, Se, Te) the weaker its bonds with hydrogen and more easily $H^{\oplus}$ gets released in aqueous solution.

f. $\overset{4+}{H_2SO_3} > \overset{4+}{H_2SeO_3} > \overset{4+}{H_2TeO_3}$

[All are oxoacids of group 16]

Same explanation as in part (d) above.

Alternatively: Increasing size and decreasing EN from S to Te, withdraws electron from O–H bond towards itself (more in H_2SO_3), thus facilitating the release of proton.

g. $\overset{6+}{H_2SO_4} > \overset{4+}{H_2SeO_4} > \overset{6+}{H_2TeO_4}$

[All are oxoacids of group 16]

Same explanation as in part (f) above.

h. HI > HBr > HCl > HF [These are hydrogen halides]

According to decreasing order of EN, F > Cl > Br > I, the acidic strength should be H–F > HCl > H–Br > HI. The more the EN of the central atom, the more is the withdrawal of electrons from H to X towards itself, thus facilitating the release of proton.

But the observed order of the acidic strength is as given above, i.e. HI > HBr > HCl > HF.

The larger the size of X (I, Br, Cl, F), the weaker its bonds with hydrogen and more easily $H^{\oplus}$ ion is released in aqueous solution. Hence the order is as given as above.

i. HO–Cl > HO–Br > HO–I. [All are oxoacids of group 17]

Decreasing order of EN of halogens is as

F > Cl > Br > I

More the EN of the halogens, more is the withdrawal of electrons from O to H bonds towards itself, thus facilitating the release of proton.

j. $\overset{5+}{P_4O_{10}} > \overset{4+}{SiO_2} > \overset{3+}{Al_2O_3} > \overset{2+}{MgO}$

Same explanation is in part (a) above.

k. $\overset{3+}{AlCl_3} > \overset{2+}{BeCl_2} > \overset{2+}{MgCl_2} > \overset{1+}{LiCl}$

$\xrightarrow{\text{Increasing pH}}$

$\xrightarrow{\text{Decreasing acidic character}}$

According to Fajans' rule, higher the charge (+ve or –ve), more is the covalent, more is the acidic character, and less is its pH.

In case of $BeCl_2$, both have +2 or –2 charge, but the size of Be^{2+} < size of Mg^{2+}, so $BeCl_2$ is more covalent than $MgCl_2$, and hence more acidic. Thus pH of $BeCl_2$ < pH of $MgCl_2$. Hence the order is as given above.

6. a. $\underbrace{\overset{1+}{Cs_2O} > \overset{1+}{K_2O}}_{\text{Group 1}} > \underbrace{\overset{2+}{SrO} > \overset{2+}{MgO}}_{\text{Group 2}} > \underbrace{\overset{2+}{NiO}}_{\text{Group 10 Transition element}}$

Generally basic strength increases down the group (↓) and decreases along the period (→).

Therefore, oxides of group 1 elements are more basic than that of group 2 elements.

Alternatively: According to Fajans' rule, small charge on the ions (+ve or –ve), large cation and small anion, the more is the ionic compound (reverse of covalent nature) and thus more basic is the compound.

Both MgO and NiO have same charge, but size of Mg^{2+} > size of Ni^{2+}.

Alternatively: Increasing electropositive nature of the element makes their oxides more basic. Mg is more electropositive than Ni (*s*-block elements are more electropositive than transition elements).

b. $CsOH > RbOH > KOH > NaOH > LiOH$

All of these hydroxides belong to group 1, and basic character increases down the group (↓).

c. $Ba(OH)_2 > Ca(OH)_2 > Mg(OH)_2 > Be(OH)_2$

All of these hydroxides belong to group 2, and the basic character increases down the group (↓).

d. $\ddot{N}H_3 > \ddot{P}H_3 > \ddot{A}sH_3 > \ddot{S}bH_3$

Note: These are not oxides or hydroxides but hydrides of group 15.

The basic character of these hydrides is based on the availability of lone pair electron on the central atom for donation to the electron-deficient compounds (Lewis acid), e.g.,

$$\underset{\substack{(e^- \text{ rich})\\(\text{Lewis base})}}{H_3N:} \longrightarrow \underset{\substack{(e^- \text{ deficient})\\(\text{Lewis acid})}}{AlCl_3}$$

The basic character of the hydrides decreases down the group (↓). Since the size of N atom is small, the lone pair of electrons is distributed over a small volume. As a result, electron density on N is high and hence $\ddot{N}H_3$ is strongly basic.

Down the group, the size of the atoms (P, As, Sb and Bi) goes on increasing and the lone pair of electrons is distributed over a large volume. As a result, electron density decreases and therefore the basic strength of their respective hydrides keeps on decreasing.

e. $$\frac{\overset{1+}{Li_2O}}{\text{Group 1}} > \frac{\overset{2+}{BeO}}{\text{Group 2}} > \frac{\overset{3+}{B_2O_3}}{\text{Group 3}} > \frac{\overset{4+}{CO_2}}{\text{Group 4}}$$

(All belong to the 2nd period)

Basic character decreases along the period (→).

Alternatively: For explanation of basic character/acidic character by Fajans' rule, refer as given in part (b) above.

f. $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

The stronger the acid, the weaker is its conjugate base and vice versa.

Acidic strength: HI > HBr > HCl > HI [refer to Question 5 (h) above].

Basic strength: $I^{\ominus} < Br^{\ominus} < Cl^{\ominus} < F^{\ominus}$.

Hence the order is as given above.

g. $\overset{\ominus}{\ddot{C}}H_3 > \overset{\ominus}{\ddot{N}}H_2 > \overset{\ominus}{\ddot{O}}H > \overset{\ominus}{F}$

Acidic strength: $HF > H_2O > NH_3 > CH_4$

Basic strength: $F^{\ominus} < \overset{\ominus}{\ddot{O}}H < \overset{\ominus}{\ddot{N}}H_2 < \overset{\ominus}{\ddot{C}}H_3$

Alternatively: The more EN the atom, the lesser is its tendency to give a lone pair of electrons.

Decreasing order of EN: F > O > N > C.

Hence the order is as given above.

h. $\overset{1+}{Tl_2O} > \overset{3+}{Tl_2O_3} > \overset{3+}{Ga_2O_3} > \overset{3+}{Al_2O_3}$ [All belong to group 13]

According to Fajans' rule, small charge, large cation and small anion, the more the ionic character and thus the more basic is the compound.

Hence the order is as given above.

7. a. $\overset{2+}{BaCl_2} > \overset{2+}{SrCl_2} > \overset{2+}{CaCl_2} > \overset{2+}{MgCl_2} > \overset{2+}{BeCl_2}$

[All belong to group 2]

According to Fajans' rule, small charge, large cation and small anion, the more is the ionic character.

Thus ionic character increases down the group (↓).

Alternatively: Increase in electropositivity of the element increases the ionic character.

b. $\overset{3+}{GaCl_3} > \overset{3+}{AlCl_3} > \overset{3+}{BCl_3}$ [All belong to group 13]

Same explanation as in part (a) above.

c. $\overset{2+}{VCl_2} > \overset{3+}{VCl_3} > \overset{4+}{VCl_2} > \overset{5+}{VOCl_3}$

Same explanation as in part (a) above.

d. $\overset{1+}{CsBr} > \overset{1+}{RbBr} > \overset{1+}{KBr} > \overset{1+}{NaBr} > \overset{1+}{LiBr}$

[All belong to group 1]

Same explanation as in part (a) above.

e. $\overset{\oplus\ \ominus}{Li\,F} > \overset{+1\times2}{K_2}O^{-2} > \overset{3+}{Cl}F_3 > \overset{4+}{SO_2} > N_2$ [Same explanation as in part (a) above]

f. MnO is the most ionic. Apply Fajans' rule.

The lesser the charge, the more is the ionic character.
Therefore, decreasing order of ionic character:

$\overset{2+}{MnO} > \overset{5+}{P_2O_5} > \overset{6+}{CrO_3} > \overset{7+}{Mn_2O_7}$

8. a. $\overset{1+}{Li}I > \overset{1+}{Li}Br > \overset{1+}{Li}Cl$. [All belong to group 1]

According to Fajans' rule, high charge on the ions, small cation, large anion, the more is the covalent character.

Hence the order is as given above.

b. $\overset{4+}{TiCl_4} > \overset{3+}{TiCl_3} > \overset{2+}{TiCl_2}$

Same explanation as in part (a) given above.

c. $\overset{7+}{I}F_7 > \overset{6+}{S}F_6 > \overset{5+}{P}Cl_5 > \overset{4+}{Si}Cl_4 > \overset{3+}{Al}Cl_3 > \overset{2+}{Mg}Cl_2 > \overset{\oplus}{Na}Cl$
Same explanation as in part (a) given above.

d. $\overset{4+}{C}Cl_4 > \overset{4+}{Si}Cl_4 > \overset{4+}{Ge}Cl_4 > \overset{4+}{Sn}Cl_4 > \overset{4+}{Pb}Cl_4$
Same explanation as in part (a) given above.

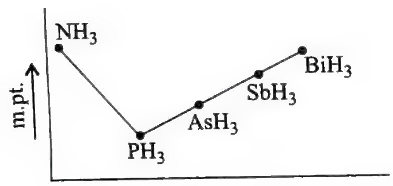
e. $\overset{4+}{C}I_4 > \overset{4+}{C}Br_4 > \overset{4+}{C}Cl_4$
Same explanation as in part (a) given above.

f. $\overset{3+}{Lu}Cl_3 > \overset{3+}{Gd}Cl_3 > \overset{3+}{Ce}Cl_3 > \overset{3+}{La}Cl_3$ [All belong to lanthanides series]

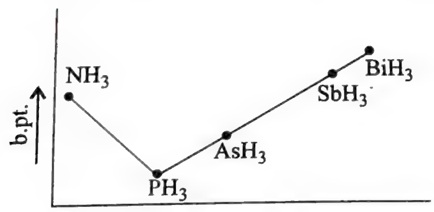
In lanthanides, the size of cation decreases in that series (due to lanthianide contraction).
$\therefore$ Size of $La^{3+} > Ce^{3+} > Gd^{3+} > Lu^{3+}$
Hence according to Fajans' rule, the order is as given above.

9. a. $Li > Na > K > Rb > Cs$ [All belong to group 1]
The melting (or boiling) point decreases down group 1, since the metallic bonding decreases but metallic character increases down the group (↓).

b. Hydrides of group 15.



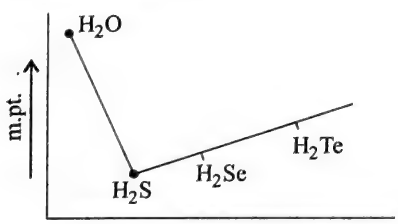
	NH_3 >	BiH_3 >	SbH_3 >	AsH_3 >	PH_3
m.pt. (K)	195.2	—	185	156.7	139.5



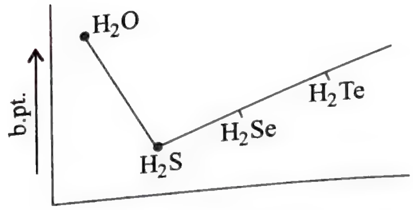
	BiH_3 >	SbH_3 >	NH_3 >	AsH_3 >	PH_3
b.pt. (K)	290	254.6	238.6	210.6	185

For explanation, refer to Chapter 2.

c. Hydrides of group 16

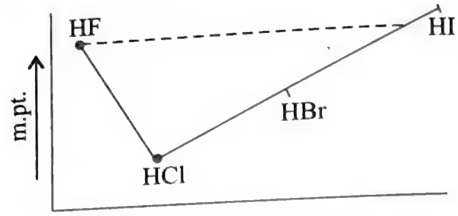


$H_2O > H_2Te > H_2Se > H_2S$
m.pt. (K) $273 > 222 > 208 > 188$

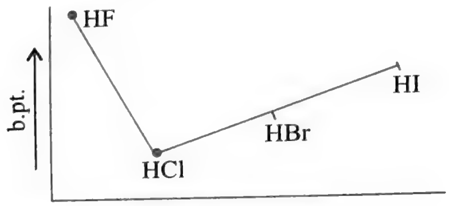


$H_2O > H_2Te > H_2Se > H_2S$
b.pt. (K) $373 > 269 > 232 > 213.$
For explanation, refer to Chapter 2.

d. Hydrides of group 17



$HI > HF > HBr > HCl$
m.pt. (K) $222 > 190 > 185 > 159$



$HF > HI > HBr > HCl$
b.pt. (K) $293 > 238 > 206 > 189$
For explanation, refer to Chapter 2.

e. Melting point of $H_2O > NH_3 > HF$
m.pt. (K) $273 > 195.2 > 190$
Boiling point of $H_2O > HF > NH_3$
b.pt. (K) $373 > 293 > 238.5$
For explanation, refer to Chapter 2.

f. m.pt. $KF > KCl > KBr > KI$
The more ionic a compound, the higher is the m.p Therefore according to Fajans' rule, the more in th ionic character. Hence the m.pt. are as given above.

g. m.pt. $CaF_2 > CaCl_2 > CaBr_2 > CaI_2$
Same explanation as given in part (f) above.

h. $\overset{1+}{Li}Br > \overset{1+}{Li}I > \overset{2+}{Be}Br_2 > \overset{3+}{B}Br_3$
Same explanation according to Fajan's rule.

10. a. **All of them belong to 3*d* series of transition element**
$Cr^{2+} > Co^{2+} > Ni^{2+} > Ti^{3+} > Zn^{2+}$
(The more the number of unpaired e^-'s, the higher the magnetic moment) and are coloured also.

Valence electronic configuration		n = unpaired e^-	Colour
Ti (Z = 22) .... $3d^2\ 4s^2$	$Ti^{3+} = 3d^1\ 4s^0$	$n = 1$	All coloured
Cr (Z = 24) .... $3d^5\ 4s^1$	$Cr^{2+} = 3d^4\ 4s^0$	$n = 4$	
Co (Z = 27) .... $3d^7\ 4s^2$	$Co^{2+} = 3d^7\ 4s^0$ ⇅ ⇅ ↑ ↑ ↑	$n = 3$	
Ni (Z = 28) .... $3d^8\ 4s^2$	$Ni^{2+} = 3d^8\ 4s^0$ ⇅ ⇅ ⇅ ↑ ↑	$n = 2$	
Zn (Z = 30) .... $3d^{10}\ 4s^2$	$Zn^{2+} = 3d^{10}\ 4s^0$	$n = 0$	Colourless

b. $N > O > Al > Ca$ ($n = 3, 2, 1, 0$)

Valence electronic configuration		
Ca (Z = 20) .... $4s^2$	$n = 0$	Colourless
Al .... $3s^2\ 3p^1$	$n = 1$	All coloured
N (Z = 7) .... $2s^2\ 2p^3$	$n = 3$	
O (Z = 8) .... $2s^2\ 2p^4$ ⇅ ↑ ↑	$n = 2$	

c. All of them belong to $3d$ transition element.

$Cr > Mn > Fe > V > Ti > Sc$ ($n = 6, 5, 4, 3, 2, 1$)

Valence electronic configuration:

Sc (Z = 21) .... $3d^1\ 4s^2$ $\Rightarrow n = 1$
Ti (Z = 22) .... $3d^2\ 4s^2$ $\Rightarrow n = 2$
V (Z = 23) .... $3d^3\ 4s^2$ $\Rightarrow n = 3$
Cr (Z = 24) .... $3d^5\ 4s^1$ $\Rightarrow n = 6$
Mn (Z = 25) .... $3d^5\ 4s^2$ $\Rightarrow n = 5$
Fe (Z = 26) .... $3d^6\ 4s^2$
⇅ ↑ ↑ ↑ ↑ $\Rightarrow n = 4$

d. $Mn^{\oplus} > Cr^{\oplus} = Fe^{\oplus} > V^{\oplus} > Ti^{\oplus} > Sc^{\oplus}$
($n = 6, 5, 5, 4, 3, 2$)

Valence electronic configuration [as given in part (c) above]

$\therefore$ $Sc^{\oplus}$ = ... $3d^1\ 4s^1$ $\Rightarrow n = 2$
$Ti^{\oplus}$ = ... $3d^2\ 4s^1$ $\Rightarrow n = 3$
$V^{\oplus}$ = ... $3d^3\ 4s^1$ $\Rightarrow n = 4$
$Cr^{\oplus}$ = ... $3d^5\ 4s^0$ $\Rightarrow n = 5$
$Mn^{\oplus}$ = ... $3d^5\ 4s^1$ $\Rightarrow n = 6$
$Fe^{\oplus}$ = ... $3d^6\ 4s^1$ $\Rightarrow n = 5$
($n = 4$) ($n = 1$)

All are coloured

e. $Mn^{2+} > Cr^{2+} > = Fe^{2+} > V^{2+} > Ti^{2+} > Sc^{2+}$
($n = 5, 4, 4, 3, 2, 1$)

Valence electronic configuration as given in part (c) above

Sc^{2+} = ... $3d^1\ 4s^0$ $\Rightarrow n = 1$
Ti^{2+} = ... $3d^2\ 4s^0$ $\Rightarrow n = 2$
V^{2+} = ... $3d^3\ 4s^0$ $\Rightarrow n = 3$
Cr^{2+} = ... $3d^4\ 4s^0$ $\Rightarrow n = 4$
Mn^{2+} = ... $3d^5\ 4s^0$ $\Rightarrow n = 5$
Fe^{2+} = ... $3d^6\ 4s^0$ $\Rightarrow n = 4$

All are coloured

f. $Fe^{3+} > Mn^{3+} > Cr^{3+} > V^{3+} > Ti^{3+} > Sc^{3+}$ ($n = 5, 4, 3, 2, 1, 0$)

Valence electronic configuration as given in part (c) above

Sc^{3+} = ... $3d^0\ 4s^0$ $\Rightarrow n = 0$ Colourless
Ti^{3+} = ... $3d^1\ 4s^0$ $\Rightarrow n = 1$
V^{3+} = ... $3d^2\ 4s^0$ $\Rightarrow n = 2$
Cr^{3+} = ... $3d^3\ 4s^0$ $\Rightarrow n = 3$
Mn^{3+} = ... $3d^4\ 4s^0$ $\Rightarrow n = 4$
Fe^{3+} = ... $3d^5\ 4s^0$ $\Rightarrow n = 5$

All are coloured

g. $P > Si = S > Al = Cl$

Valence electronic configuration:

Al(Z = 13) .... $3s^2\ 3p^1$ $n = 1$
Si(Z = 14) .... $3s^2\ 3p^2$ $n = 2$
P(Z = 15) .... $3s^2\ 3p^3$ $n = 3$
S(Z = 16) .... $3s^2\ 3p^4$
⇅ ↑ ↑ $n = 2$
Cl(Z = 17) .... $3s^2\ 3p^5$
⇅ ⇅ ↑ $n = 1$

All are coloured

11. a. $NH_3 > PH_3 > AsH_3$
$107.5° > 93.3° > 91.8°$
For explanation, refer to Section 1.16(3)(a).

b. $H_2O > H_2S > H_2Se$
$104.5° > 92.5° > 91°$
For explanation, refer to Section 1.16, Point 3(a) (Explanation)

c. $NF_3 > PH_3 > AsF_3$
$102° > 93.3° > 90°$

The increasing size (from $N \rightarrow P \rightarrow As$) and decreasing EN (from $N \rightarrow P \rightarrow As$) of the central atom, permit the bonding electrons to be drawn out further, thus decreases repulsion between bonding pairs.

d. $NCl_3 > NF_3$

For explanation, refer to Section 1.16, Point 3(a)(ii).

e. $NO_2^{\oplus} > NO_2 > NO_2^{\ominus}$
$180° > 134° > 115°$
For explanation, refer to Section1.16, Point 3(a)(v).

f. $NH_3 > NF_3$. For explanation, refer to Section 1.16, Point 3(a)(iii).

g. $PF_3 > PH_3$. For explanation, refer to Section 1.16, Point 3(a)(iii).

h. State of hybridisation is also used for determination of bond angle, refer to Section 1.16, Point 3(a)(v).

$HC \equiv CH$ (180°) (sp) (Linear) > BF_3 (120°) (sp^2) (Planar) > CH_4 (109.5°) (sp^3) (Tetrahedral)

> NH_3 (107°) Pyramidal, sp^3 but there is repulsion between lone pair and bond pair. > H_2O (104.5°) V shape, sp^3 but more repulsion between lone pair and bond pair.

i. $O=C=O\ (180^\circ)$ > $CH_4\ (109.5^\circ)$

sp (Linear) — sp^3 (Tetrahedral)

$NH_3\ (107^\circ)$ > $H_2O\ (104.5^\circ)$

sp^3 (Pyramidal) — sp^3 (V shape)

Same explanation as given in part (h) above.

j.

$\overset{\oplus}{N}H_4\ (109.5^\circ) > \ddot{N}H_3\ (107^\circ) > \ddot{S}Cl_2\ (104^\circ) > PCl_5$

(sp^3)	(sp^3)	(sp^3)	(sp^3d)
Tetrahedral	Pyramidal	V-shape, similar to H_2O structure	Trigonal bi-pyramid 120° and 90°

Same explanation as given in part (h) above.

k. $NO_2^{\oplus}\ (180^\circ) > NO_2(134^\circ) > NO_3^{\ominus}(120^\circ) > NO_2^{\ominus}(115^\circ)$

Linear. (sp) — One unshared electron, sp^2 — sp^2 and have 3 resonating structure — one lone pair, sp^2

For explanation, refer to Section 1.16, Point 3(a)(v).

l. BF_3 > SiH_4 > $\ddot{N}H_3$ > $H_2\ddot{S}$:

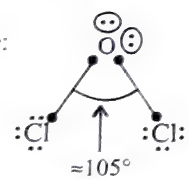
sp^2	sp^3	sp^3	sp^3
Planar 120°	sp^3 Tetrahedral 109.5°	sp^3 Tetrahedral 107° Due to repulsion between lp and bp	sp^3 Tetrahedral 104.5° Due to repulsion between lp and lp

m. i. $Cl_2\ddot{O}: \Rightarrow$ Hybridisation $= 2\ bp + 2\ lp = 4 = sp^3$.

OR

$$\text{Hybridisation} = \frac{1}{2}(V+M) = \frac{1}{2}(6+2) = 4 = sp^3$$

Structure:



Due to lp–lp repulsion the bond angle decreases from the expected 109.5° to $\approx 105^\circ$ (like H_2O).

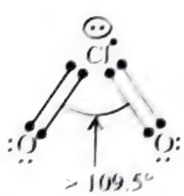
ii. $.\ddot{C}lO_2 \Rightarrow$ Hybridisation $= 2\ bp + 1\ lp + 1e^- = 4 = sp^3$.

OR

$$\text{Hybridisation} = \frac{1}{2}(V + M + \text{unpaired } e^-)$$

$$= \frac{1}{2}(7+0+1) = 4 = sp^3$$

Structure:

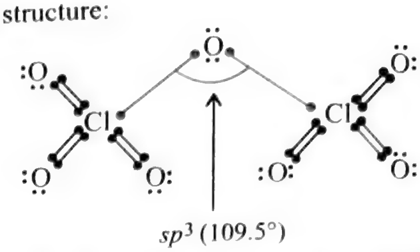


Since there are only three non-bonding e^-'s on the central atom in ClO_2, the repulsion for the bonded pairs is less than that in Cl_2O and the angle between the bonds is greater in ClO_2.

Moreover, the resonance of single electron among the bonding and non-bonding orbitals on the central atom lead to angle somewhat greater than the tetrahedral angle (i.e. $>109.5^\circ$).

The shorter bond length (O–Cl) in ClO_2 results from resonance, with the unpaired e^-'s on the Cl or O atom.

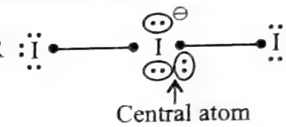
iii. Cl_2O_7 structure:



The tetrahedral angle about the Cl atoms is as expected (109.5°).

The angle about the central O atom is also expected for an sp^3 hybridised central atom with two of the pairs of electrons bonded to other atoms.

iv. $I_3^{\ominus}$ OR



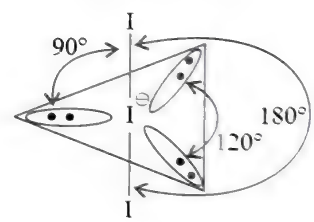
Hybridisation $= 2\ bp + 3\ lp = 5 = sp^3d$

OR

$$\text{Hybridisation} = \frac{1}{2} = (V + M + (\text{negative charge})$$

$$= \frac{1}{2}(7+2+1) = 5 = sp^3d$$

$$= \text{Trigonal bipyramid (Tbp)}$$



The linear orientation of $I_3^{\ominus}$ results from the five pairs of electrons being oriented in Tbp geometry about the central atom. The two bonding pairs repel less than the non-bonding pairs (i.e. lp's) and so are most stable at the **apical positions** (90° from three other pairs). Bond angle between $I–I^{\ominus}–I$ is 180°. So the decreasing order of bond angle is

$I_3^{\ominus}\ (180^\circ) > ClO_2\ (>109.5^\circ) > Cl_2O_7\ (109.5^\circ) > Cl_2O\ (\approx 105^\circ)$

12. a. $BaF_2 > CaF_2 > MgF_2 > BeF_2$

b. $Ba(OH)_2 > Ca(OH)_2 > Mg(OH)_2 > Be(OH)_2$

For explanation of (a) and (b), refer to Section 1.27.1, Point 10(b).

Note: Lattice energy variation is more dominating than the variation in hydration energy.

c. $BeCO_3 > MgCO_3 > CaCO_3 > BaCO_3$

d. $BeSO_4 > MgSO_4 > CaSO_4 > BaSO_4$

e. $Be(HCO_3)_2 > Mg(HCO_3)_2 > Ca(HCO_3)_2 > Ba(HCO_3)_2$

Note: Down the group (↓), the lattice energies of carbonates, sulphates and bicarbonates do not decrease much while the degree of hydration of the metal ions decreases significantly leading to decreased solubility.

For detailed explanation of (c), (d) and (e), refer to Section 1.27.1, Point 10(c).

f. $\overset{1+}{NaCl} > \overset{2+}{MgCl_2} > \overset{3+}{AlCl_3} > \overset{4+}{CCl_4}$

According to Fajans' rule, the more ionic a compound the more is soluble in water.
Hence, the order is as given above.

g. $\overset{1+}{NaCl} > \overset{1+}{CuCl}$

According to Fajans' rule, NaCl is more ionic than CuCl (which is covalent).
Both have same charge, sizes of cation and anion are also same.

But $Cu^{\oplus}$ have *d*-orbitals. So CuCl is covalent and NaCl is ionic.

The more the ionic, the more is the solubility in water.
Hence, the order is as given above.

h. $H\overset{5+}{N}O_3 > H_3\overset{5+}{P}O_4 > H_3\overset{5+}{As}O_4 > H_3\overset{5+}{Sb}O_4$

(All of them belong to group 15)

According to Fajans' rule, the acidic character is given as above (Refer to solution of Question 5 (d).

The more is the acidic character, the more is the solubility in water

i. $H_2\overset{+4}{S}O_3 > H_2\overset{+4}{Se}O_3 > H_2\overset{+4}{Te}O_3 \begin{bmatrix} \text{All are oxoacids} \\ \text{of group 16} \end{bmatrix}$

Refer to solution of Question 5 (f).

13. a. Bond length: $Cl–Cl > F-F > O=O > N \equiv N$

Bond strength: $N \equiv N > O=O > F-F > Cl-Cl$

Fluorine and chlorine contain a single bond each. Chlorine involves overlap of 3*p* orbitals while fluorine involves overlap of 2*p* orbitals. Overlap of 2*p*–2*p* orbitals is stronger than 3*p*–3*p* overlap. So bond strength of $F_2 > Cl_2$ and bond length of $Cl_2 > F_2$.

Nitrogen contains triple bond and oxygen contains double bond. Triple bond is stronger than double bond.

$$\text{Bond strength} \propto \frac{1}{\text{Bond length}}$$

Hence, the order is as given above.

b. $F-F > O-O > N-N$

Same explanation as given in part (a) above.

c. $Cl_2 > Br_2 > F_2 > I_2$ (observed trend)

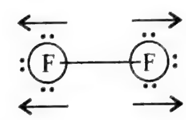
Bond enthalpy (kJ mol^{-1}) $242.6 > 192.8 > 158.8 > 151.1$

The expected trend in the bond dissociation energy should be:

$F_2 > Cl_2 > Br_2 > I_2$

Enthalpy of dissociation decreases as the bond distance increases from F_2 to I_2, due to a corresponding increase in the size of the atom down the group from F to I.

But the bond dissociation enthalpy of F_2 is however smaller than that of Cl_2 and even smaller than that of Br_2. This is due to the reason that F atom is very small and hence the electron–electron repulsions between the lone pairs of electrons are very large, e.g.



Hence, the order is as given above.

d. $HF > HCl > HBr > HI$ (Hydrides of group 17)

As the size of halogen atom increases, the strength of HX bond increases. Besides this, the decreasing per cent of ionic character from HF to HI makes the bond less stable.

e. $HClO_4 > HClO_3 > HClO_2 > HClO$

The stability is explained by increasing the number of electrons involved in the formation of σ and π bonds is going from HClO to $HClO_4$. In $ClO_4^{\ominus}$ ion, all the valence orbitals and electrons of chlorine are involved in the formation of bonds.

f. $CsOH > RbOH > KOH > NaOH > LiOH$

Down the group, according to Fajans' rule, the ionic character of hydroxides of group 1 and group 2 increases. Therefore, the more ionic a compound, the more is the thermal stablity.

g. $NH_3 > PH_3 > SbH_3 > BiH_3$ (Hydrides of group 15)

Stability of hydrides of groups 15, 16 and 17 decreases down the group (↓). SbH_3 and BiH_3 are thermally unstable whereas BiH_3 has been obtained in traces only.

Since the size of element (M) in M–H increases down the group (↓), the bond length between M and H in MH increases and the bond strength decreases down the group.

Reducing the character of hydrides of groups 15, 16 and 17 increases down the group.

Down the group (↓) the removal of H-atom increases, so the reducing character order is as given below:

Reducing character: $BiH_3 > SbH_3 > AsH_3 > PH_3 > NH_3$.

h. Thermal stability: $H_2O > H_2S > H_2Se > H_2Te$.

Reducing character: $H_2Te > H_2Se > H_2S > H_2O$.

Same explanation as in part (g) above.

i. $H_2SO_3 > H_2SeO_3 > H_2TeO_3$ (All are oxoacids).

Same explanation as in part (g) above.

j. $H_2SO_4 > H_2SeO_4 > H_2TeO_4$ (All are oxoacids).

Same explanation as in part (g) above.

k. $HIO_3 > HBrO_3 > HClO_3 > HFO_3$

Ions of these acids are stabilised due to strong *p*π–*d*π multiple bonding between full 2*p* orbitals on oxygen

and empty d-orbitals on the halogen atom. Fluorine has no d-obritals and can not form $p\pi$–$d\pi$ bonds. Thus oxoacids of fluorine are not known.

l. $LiH > NaH > KH > CsH$ (All hydrides of groups 1 and 2)

According to Fajans' rule, hydrolysis of cations depends on two factors: larger charge and smaller size favour more hydrolysis, hence, more free $H^{\oplus}$ ions.

m. $BaCO_3 > CaCO_3 > MgCO_3 > BeCO_3$.

Increasing size of cation decreases its polarising ability towards carbonate ion, (CO_3^{2-}), and thus making the compound more stable. Hence stability of carbonates of group 2 elements decreases down the group.

n. $Li\ (Z = 3) \Rightarrow 2s^1$, $\quad Li^{\ominus} \Rightarrow 2s^2$ (Full filled, most stable)

$Be\ (Z = 4) \Rightarrow 2s^2$, $\quad Be^{\ominus} \Rightarrow 2s^2, 2p^1$ (Least stable)

$B\ (Z = 5) \Rightarrow 2s^2, 2p^1, B^{\ominus} \Rightarrow 2s^2, 2p^2$

$C^{\ominus}\ (Z = 6) \Rightarrow 2s^2, 2p^2\ C^{\ominus} \Rightarrow 2s^2, 2p^3$ (Half filled, stable)

Therefore, decreasing order of stability:

$Li^{\ominus} > C^{\ominus} > B^{\ominus} > Be^{\ominus}$

14. a. $PCl_5 > SiCl_4 > AlCl_3 > MgCl_2 > CCl_4$

group 15	group 14	group 13	group 2	group 14

In covalent halides, hydrolysis occurs as a result of coordination of a water molecule to the less EN element. CCl_4 does not undergo hydrolysis as carbon cannot expand its octet to accommodate water molecules.

b. $BiCl_3 > SbCl_3 > AsCl_3 > PCl_3 > NCl_3$ (All belong to group 15)

Hydrolysis increases down the group (↓).

These trihalides are predominantly covalent with ionic character increasing down the group (↓) (Fajans' rule). The trihalides undergo hydrolysis but the product of hydrolysis depends upon the nature of the element. For example,

i. $NCl_3 + 3\,H_2O \longrightarrow NH_3 + 3\,HOCl$

OR

$NCl_3 + 4\,H_2O \longrightarrow NH_4OH + 3\,HOCl$

ii. $PCl_3 + 3\,H_2O \longrightarrow H_3PO_3 + 3\,HCl$

(Phoshorous acid)

iii. $AsCl_3 + 3\,H_2O \longrightarrow H_3AsO_3 + 3\,HCl$

iv. $SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$

(Antimony oxychloride)

OR

$SbCl_3 + H_2O \longrightarrow SbO^{\oplus} + 3Cl^{\ominus} + 2H^{\oplus}$

v. $Bi\,Cl_3 + H_2O \longrightarrow BiO^{\oplus} + 3Cl^{\ominus} + 2H^{\oplus}$

OR

$BiOCl + 2HCl$

(Bismuth oxychloride)

c. $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

Hydration of ions ∝ charge density $\left(\dfrac{\text{Charge}}{\text{Size}}\ \text{ratio}\right)$

Hydration of ions decreases down the group (↓) and increases along the period (→).

d. $Li^{\oplus} > Na^{\oplus} > K^{\oplus} > Rb^{\oplus} > Cs^{\oplus}$

Same explanation as given in part (c) above.

The more is the extent of hydration, the more negative hydration energy is released.

e. $Ca^{2+} > Ba^{2+} > K^{\oplus} > Cs^{\oplus}$

Hydration energy of group 2 ions > Hydration energy of group 1 ions [as explained in part (c) above].

15. a. $BBr_3 > BCl_3 > BF_3$.

Besides σ bond between boron and hologen atoms, there exists additional $p\pi$–$p\pi$ bond between the two atoms resulting from back-donation of electrons from fluorine to boron (back bonding).

The tendency to form $p\pi$–$p\pi$ bond is maximum in BF_3 ($2\,p\pi - 2\,p\pi$ back bonding) and falls rapidly on passing to BCl_3 ($2\,p\pi - 3\,p\pi$ back bonding) and BBr_3 ($2\,p\pi - 4\,p\pi$ back bonding). The tendency to accept electron pair, therefore increases from BF_3 to BBr_3.

b. $AlCl_3 > GaCl_3 > InCl_3$. With increase in size of elements of group 13, the tendency to accept electron pair is decreased.

16. a. $\overset{+4}{PbCl_4} > \overset{+4}{SnCl_4} > \overset{+4}{GeCl_4}$ (All belong to group 14)

Due to inert pair effect, the stability of element in group 14, from +4 oxidation state to +2 oxidation state increases down the group (↓), e.g.

$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}$ (Reduction and hence acts as oxidising agent).

b. $F > Cl > Br > I$ (All belong to group 17)

Reduction potential $[E^{\ominus}_{F/F^{\ominus}(aq)}]$ of halogens decreases down the group, so oxidising power also decreases.

c. $O > S > Se > Te$ (All belong to group 16)

Same expalnation as given in part (b) above.

d. $BrO_4^{\ominus} > IO_4^{\ominus} > ClO_4^{\ominus}$

This is due to their reduction potential values.

i. $BrO_4^{\ominus} + 2H^{\oplus} + 2e^- \longrightarrow BrO_3^{\ominus} + H_2O; E^{\ominus} = 1.74\ V$

ii. $IO_4^{\ominus} + 2H^{\oplus} + 2e^- \longrightarrow IO_3^{\ominus} + H_2O;\ E^{\ominus} = 1.65V$

iii. $ClO_4^{\ominus} + 2H^{\oplus} + 2e^- \longrightarrow ClO_3^{\ominus} + H_2O;$ $E^{\ominus} = 1.19V$

Although among perhalates, $BrO_4^{\ominus}$ is the strongest oxidising agent, yet it is a weaker oxidising agent than F_2. This is because $BrO_4^{\ominus}$ (perbromate) and $HBrO_4$ (per bromic acid) can be obtained by the oxidation of bromates $(BrO_4^{\ominus})$ by F_2 in alkaline solution

$BrO_3^{\ominus} + F_2 + 2\overset{\ominus}{O}H \rightarrow BrO_4^{\ominus} + 2F^{\ominus} + H_2O$

e. $ClO^{\ominus} > BrO^{\ominus} > IO^{\ominus}$

As the size of the halogen increases, the thermal stability of the O–X bond increases and the oxidising power of $XO^{\ominus}$ decreases, as shown by their reduction potential values.

$$ClO^{\ominus} + 2H^{\oplus} + 2e^{-} \longrightarrow \frac{1}{2}Cl_2 + H_2O; E^{\ominus} = 1.61\ V$$

$$BrO^{\ominus} + 2H^{\oplus} + 2e^{-} \longrightarrow \frac{1}{2}Br_2 + H_2O; E^{\ominus} = 1.60\ V$$

$$IO^{\ominus} + 2H^{\oplus} + 2e^{-} \longrightarrow \frac{1}{2}I_2 + H_2O; E^{\ominus} = 1.44\ V$$

f. $GeCl_2 > SnCl_2 > PbCl_2$ (All belong to group 14)

The stability of element in +2 oxidation state increases down the group 14 (↓). This is due to inert pair effect [As explained in part (a) above].

g. $HI > HBr > HCl > HF$

The reducing power of HX acids depends upon the ease with which it decomposes to give H_2 and X_2.

$2\,HX \rightarrow H_2 + X_2$.

Greater the bond dissociation energy, the more stable is the HX acid and hence weaker is the reducing agent. Bond dissociation enery of HX is as:

$HF > HCl > HBr > HI$

and hence the reducing power of HX is as shown above.

17. a. $F > O > N > Cl > S$

H-bonding ∝ EN of the element and

$$\text{H-bonding} \propto \frac{1}{\text{size of the element}}$$

The decreasing order of EN is $F > O > N > Cl > S$.

The decreasing order of size is $F < O < N < Cl < S$.

High EN and small size of the element makes hydrogen bonding more strong.

b. $Cs > Rb > K > Na > Li$ (All belong to group 1)

The reactivity increases down the group 1 (↓) due to decrease in ionisation energy down the group 1 (↓).

c. $Ba > Sr > Ca > Mg > Be$ (All belong to group 2).

Same explanation as given in part (b) above.

d. $Cs > Rb > K > Na > Li$ (All belong to group 1)

The ease of formation of hydrides increases down the group 1 (↓).

e. $Ba > Sr > Ca > Mg > Be$ (All belong to group 2).

The ease of formation of oxides increases down the group 2 (↓).

f. $C > Si > Sn$ (All belong to group 14).

The number of hybrid orbitals and ease with which these are formed decreases down the group 14 (↓), i.e. from C to Pb.

g. $HIO_4 > ICl > I_2 > HI$

The oxidation of iodine in $\overset{7+}{HIO_4}, \overset{1+}{ICl}, \overset{0}{I_2}$ and $\overset{1-}{HI}$ are +7, +1, 0 and −1 respectively

h. $N > P > As > Sb > Bi$ (All belong to group 15).

Stability of lower oxidation state (i.e. from + 5 to + 3 in group 15) increases down the group 15 (↓). This is due to inert pair effect.

i. $PoH_2 > H_2Te > H_2Se > H_2O$

(All belong to group 16)

Poisonous nature increases down the group 16 (↓). Po is radioactive and is most poisonous.

j. $F_2 > Cl_2 > Br_2 > I_2$ (All belong to group 17)

F_2 is most reactive of all the halogens, because F_2 has higher reduction potential than other halogens. The reduction potential $\left[E^{\ominus}_{X_2/2X^{\ominus}(aq)}\right]$ decreases down the group 17 (↓).

k. $Li > Na > Cu > Fe$

(*s*-block) (*d*-block)5

s-block elements are more electropositive than *d*-block elements. But the electropositive character in *s*-block elements increases down the group. So the electropositive character of Na should be more than Li. But this is an exceptional case, Li is more electropositive in aqueous solution (refer to Section 1.27.1).

l. $Au > Pb > Fe > Al$ (Atomic weight of Au, Pb, Fe and Al are 196.97, 207.19, 55.85 and 26.98 respectively)

Increasing atomic mass increases the density.

So, the density of Pb should be greater than that of Au. But Au belongs to 4*d*-transition element series and the size is less than that of Pb. So, the density of Au > the density of Pb.

m.

	CO_2 >	H_2S >	O_2 >	NH_3 >	H_2
[Molecular weight ($g\ mol^{-1}$)]	44	34	32	17	2

Increasing molecular masses increases the density.

CONCEPT APPLICATION EXERCISE 1.3

1. Arrange the following in order of decreasing ionic character.
   a. $Cl\,F_3$, SO_2, N_2, K_2O and LiF
   b. C – H, F – H, Br – H, Na – I, K – F and Li –Cl
   c. AlF_3, $AlCl_3$, $AlBr_3$
2. Arrange the following in order of decreasing bond angle.
   a. CO_2, H_2O, CH_4
   b. SO_4^{2-}, SO_3^{2-}
3. $Ca\,CO_3$ dissolves in HCl but not in water. Why?
4. Why MgO exist as $Mg^{2+}O^{2-}$ not as $Mg^{\oplus}O^{\ominus}$ whereas the formation of Mg^{2+} from Mg requires more energy than formation of $Mg^{\oplus}$ and formation of $O^{\ominus}$ from O is exothermic whereas the formation of O^{2-} is endothermic.

5. Anhydrous $AlCl_3$ is covalent from the data given below, predict whether it would remain covalent or become ionic in aqueous solution
IE_1 of Al = 5140 kJ mol^{-1}
$\Delta_{hyd}H^{\circ}(Al^{3+}) = -4665$ kJ mol^{-1}
$\Delta_{hyd}H^{\circ}(Cl^{-}) = -380$ kJ mol^{-1}
6. Which compound for each of the following pairs is more ionic and why?
   a. $BeBr_2$ or $MgBr_2$ b. $PbCl_2$ or $PbCl_4$
   c. AgBr or AgI d. CuO or CuS
7. NaBr gives pale yellow precipitate with $AgNO_3$ solution but CBr_4 does not. Why?
8. Copper is conducting as such while Cu SO_4 is conducting only in molten state or in aqueous solution. Why?
9. Explain the observed bond angle order.
Cl_2O (110.8°) > H_2O (104.5°) > F_2O (103.2°)
10. $\overset{\oplus}{NH_4}$ has bond angle identical to CH_4 but NH_3 has different bond angle. Why?
11. Electronegativities of F, O, N, Cl, H are 4.0, 3.5, 3.2 and 2.1 respectively. In which atoms there is strongest bond.
12. The IE_1 of Li is 5.4 eV and IE_1 of H is 13.6 eV. Calculate the charge acting on the outermost electron of Li atom.
13. a. The melting point of KBr is higher than that of AgBr though the cyrstal radii of $Ag^{\oplus}$ and $K^{\oplus}$ ions are almost the same. Explain.
    b. $SnCl_2$ is solid but $SnCl_4$ is liquid. Why?

Solved Examples

Example 1.1

Predict the group number and block to which the given elements belong.
A (Z = 9), B (Z = 20), C (Z = 29), D (Z = 36) and E (Z = 58).

Sol. A = $1s^2$, $\boxed{2s^2, 2p^5}$ (Z = 9)

The last electron is in the 2*p*-orbital, therefore it belongs to *p*-block elements.

∴ Group number = 10 + 7 = 17

Period of the element = 2nd [Number of the principal quantum number of the valence shell]

Hence A = group 17 and 2nd period.

B = $1s^2$, $2s^2 2p^6$, $3s^2 3p^6$, $\boxed{4s^2}$ (Z = 20)

The last electron is in the 4*s*-orbital, therefore it belongs to *s*-block elements.

∴ Group number = 2 (Number of electrons in the valence shell)

Period = 4th (Number of the principal quantum number of the valence shell)

C = $1s^2$, $2s^2 2p^6$, $3s^2 3p^6$, $\boxed{4s^1, 3d^{10}}$ (Z = 29)

The last electron is in the 3*d*-orbital, therefore it belongs to *d*-block elements.

∴ Group number = 11th [Number of electrons in the penultimate shell (i.e. in 3*d*) and valence shell (i.e. in 4*s*) = 10 + 1 = 11]

Period = 4th (Number of the principal quantam number of the valence shell)

D = $1s^2$, $2s^2 2p^6$, $3s^2 3p^6\ 3d^{10}$, $\boxed{4s^2\ 4p^6}$ (Z = 36)

The last electron is in the 4*p*-orbital, therefore it belongs to *p*-block elements.

∴ Group number = 10 + 8 = 18

Period = 4th (Number of the principal quantum number of the valence shell)

E = $1s^2$, $2s^2 2p^6$, $3s^2 3p^6\ 3d^{10}$, $4s^2 4p^6\ 4d^{10}$, $5s^2 5p^6$, $\boxed{6s^2, 4f^2}$ (Z = 58)

The last electron is in the 4*f*-orbital, therefore it belongs to *f*-block elements.

Note: The filling of 4*f*-orbitals occurs only when one electron has already entered 5*d*-orbital. Therefore, *E* belongs to *f*-block elements and not to *d*-block elements.

Since it belongs to lanthanides series, therefore as such it does not have any group number.

Note: But all lanthanides and actinides belong to group 3 (or III B).

However, its period = 6th [Number of the principal quantum number of the valence shell]

Example 1.2

IE_1 (first ionisation energy) and IE_2 (second ionisation energy) of a few elements are given below:

Elements	A	B	C	D
IE_1 (kJ mol^{-1})	2370	520	900	1680
IE_2 (kJ mol^{-1})	5250	7300	1760	3380

Which of the above elements is likely to be:
a. a reactive metal
b. a reactive non-metal
c. a noble gas
d. a metal forming binary halide (MX_2)

Sol.
a. B is reactive metal since it has minimum IE_1.
b. D is reactive non-metal since it has second minimum IE_1.
c. A is noble gas since it has maximum IE_1.
d. C forms MX_2. Since IE_2 of C is the least.

EXAMPLE 1.3

Identify the three elements A, B and C from the data given below:
a. The elements have successive atomic numbers.
b. A forms a stable anion, $A^{\ominus}$
c. C forms a stable cation, $C^{\oplus}$

Sol. Let the atomic number of A is Z, and B must be $(Z+1)$ and C must be $(Z+2)$ since A, B and C have successive atomic numbers.

Halogens form the most stable halide anions as their octet is complete. But in halogens $Cl^{\ominus}$ is the most stable.

Whereas alkali metals form the most stable cations.

The atomic number of Cl = 17

$\therefore$ A = Chlorine ($Z = 17$)

B = Argon ($Z = 17 + 1 = 18$)

C = Potassium ($Z = 17 + 2 = 19$)

Note: 17, 18 and 19 are successive numbers.

EXAMPLE 1.4

Among the elements, Ar, Si, Na and Cl. Select an element with
a. Highest IE
b. Highest EA
c. Smallest size
d. Highest electrical conductivity

Sol. All of them belongs to the same 3rd period.
a. Highest IE = Ar (Since it is a noble gas)
b. Highest EA = Chlorine

[since EA or $\Delta_{eg}H^{\ominus}$ increases along the period ($\rightarrow$)]

(EA of Cl > F > Br > I)

c. Smallest size = Chlorine (since size decreases along the same period ($\rightarrow$))
d. Highest electrical conductivity = Sodium [alkali metals have highest conductivity]

EXAMPLE 1.5

Arrange the following in decreasing order as directed.
a. Decreasing order of EN: H, O, Al, F
b. Decreasing order of radii: Ar, Br, Ca^{2+}, Mg^{2+}
c. Decreasing order of EA: C, N, Be, F, O, Cl
d. Decreasing order of IE and EA: F, Cl, Br, I
e. Decreasing order of EN: F, N, O, Cl, S
f. Decreasing order of IE: Ne, O, Na, $Na^{\oplus}$
g. Decreasing electropositive character: Na, Cu, Zn

Sol.

a. **EN:** $\underbrace{F > O}_{\text{2nd period}} > \underbrace{Al}_{\text{3rd period}} > \underbrace{H}_{\text{1st period}}$

[EN increases along the period, $\therefore$ EN of F > O]

Aluminium (Al) belongs to 3rd period. [EN decreases down the group ($\downarrow$)]

b. **Radii:** $\underbrace{Br}_{\text{4th period}} > \underbrace{Ar}_{\text{3rd period}} > \underbrace{Ca^{2+}}_{\text{4th period}} > \underbrace{Mg^{2+}}_{\text{3rd period}}$

Although size of an atom decreases along the period ($\rightarrow$) but in a period, size of noble gas is highest.

Ar belongs to 3rd period whereas Br belongs to 4th period.

$\therefore$ Size of Br > Size of Ar

Similarly, although both Ca^{2+} and Mg^{2+} ions have same charge, but Ca belongs to 4th period and Mg belongs to 3rd period.

$\therefore$ Size of Ca^{2+} > Size of Mg^{2+}

c. **EA:** Cl > F > O > C > N > Be

Among halogens decreasing order of EA or $\Delta_{eg}H^{\ominus}$ = Cl > F > Br > I

Generally EA increases along the period ($\rightarrow$)

Therefore, order of EA should be O > $\boxed{N > C}$

But there is exception in the EA of N and C. Since N has half-filled stable configuration, so it is difficult to add electron to N as compared to C.

$\therefore$ EA of C > N

Among Be, $\boxed{C; N}$, O and F (all of them belong to 2nd period), EA of Be is the least.

Hence the order is as given above.

d. **IE:** F > Cl > Br > I [Generally IE decreases down the group ($\downarrow$)]

EA: $\boxed{Cl > F}$ > Br > I [Exception in case of Cl > F]

e. **EN:** $\underbrace{F > O}_{\text{2nd period}} > \underbrace{Cl > S}_{\text{3rd period}} > \underbrace{\boxed{N}}_{\text{2nd period}}$

Generally EN increases along the same period ($\rightarrow$).

Therefore, EN of 2nd period > EN of 3rd period. But EN of N (2nd period) is the least, and is an exception due to half-filled stable configuration.

f. **IE:** $\underbrace{Ne}_{\text{2nd period}} > \underbrace{Na^{\oplus}}_{\text{3rd period}} > \underbrace{O}_{\text{2nd period}} > \underbrace{Na}_{\text{3rd period}}$

IE increases along the same period ($\rightarrow$) and IE of noble gas (Ne) is the highest.

IE of alkali metal (Na) is less as compared to $Na^{\oplus}$ ion, since it is very difficult to remove an electron from a positive ion.

Generally, IE decreases down the group ($\downarrow$), so IE of O > Na.

Hence the order is as given above.

g. Electropositive character: Na > Zn > Cu

Group 1 is more metallic (or electropositive character) than group 2. So, Na is most metallic than Zn and Cu. Similarly, *d*-block elements have more electropositive character than *p*-block elements.

Hence the electropositive character is as given below.

Note: In the metallic character series, the electropositive character (or reducing character) is in the order

Na > Mg > Zn > Fe > Ni > Cu > Ag

Note that in metallic character series, PSBC MAZINTL CHAAP. Zn comes after s-block elements.

EXAMPLE 1.6

Predict from each set, the atom/ion which has the greatest IE_1 with explanation:

a. Cl or F
b. S or Cl
c. Ar or K
d. Xe or Kr
e. O or N
f. $Na^{\oplus}$ or Na
g. $Be^{\oplus}$ or Mg^{2+}
h. $I^{\ominus}$ or I
i. B or C
j. Ne or F
k. N, O, F
l. P, Ar, Mg
m. B, Al, Ga

Sol.

a. F [Small size, more Z_{eff}, less shielding effect, high IE_1 of F]

b. Cl [Cl has high IE_1 due to small size, high nuclear charge]

c. Ar [Ar has high IE, due to stable configuration K has low IE than Ar, because K has one more electron than Ar, and hence can easily lose this electron to acquire stable Ar configuration]

d. Kr [Kr has high IE, because of smaller size than that of Xe, and weaker shielding effect in Kr]

e. N [N has high IE_1 because an electron has to be lost from a stable half-filled electronic configuration. In case of O, loss of electron gives $O^{\oplus}$ which has stable exactly half-filled electronic configuration]

f. $Na^{\oplus}$ [$Na^{\oplus}$ has high IE_1, since an electron has to be lost from a stable inert gas configuration but in case of Na, loss of electron gives stable inert gas configuration]

g. Mg^{2+} [In case of Mg^{2+}, the electron has to be lost from the stable gas inert gas configuration, while in case of $Be^{\oplus}$, the loss of an electron gives a stable inert gas configuration. Hence IE of $Mg^{2+} > Be^{\oplus}$]

h. $I^{\ominus}$ [IE of $I^{\ominus}$ > I, because in case of $I^{\ominus}$ an electron has to be lost from inert gas configuration]

i. C [IE of C > B, because of higher muclear charge in C]

j. Ne [IE of Ne > F, because of stable inert gas configuration in Ne]

k. F [All belong to 2nd period. IE of F > N > O since F has the highest nuclear charge, and the smallest size among them]

l. Ar [All belong to 3rd period, IE of Ar > P > Mg. Ar has stable inert gas configuration]

m. B [All belong to group 13. IE_1 of B > Ga > Al (800 > 578 > 577), because of the smallest size and weaker shielding effect of B]

EXAMPLE 1.7

a. The $\Delta_{eg}H^{\ominus}$ of Br is 3.4 eV. How much energy in kcal is released when 0.8 g of Br (g) is completely converted to $Br^{\ominus}$(g) ions. (1 eV = 23. 06 kcal mol^{-1})

b. The energy released when 10^7 atoms of I (g) is converted to $I^{\ominus}$ (g) ions, is 5×10^{-13} J. Calculate $\Delta_{eg}H^{\ominus}$ of I (g) in (i) eV $atom^{-1}$ and (ii) kJ mol^{-1}.

Sol.

a. Moles of Br $= \dfrac{\text{Mass}}{\text{Atomic mass}} = \dfrac{0.8}{80} = 10^{-2}$

Energy released $= 10^{-2} \times 3.4 \text{ eV} \times 23.06$
$= 0.784$ kcal

b. i. $\Delta_{eg}H^{\ominus} = \dfrac{6.023\times10^{23}\times5\times10^{-13}}{10^7} = 30.115 \times 10^3$
$= 30115 \text{ kJ mol}^{-1}$

ii. 96.49 kJ mol^{-1} = I eV $atom^{-1}$

$\therefore \Delta_{eg}H^{\ominus} = (30115/96.49)$ eV $atom^{-1}$
$= 312.104$ eV $atom^{-1}$

EXAMPLE 1.8

Predict from each set, the element which has the more negative electron gain enthalpy ($\Delta_{eg}H^{\ominus}$). Give reasons:

a. C or Si
b. F or Cl
c. N or O
d. O or S
e. F, Cl, S, P
f. (i) [Ne] $3s^2\ 3p^5$ (ii) [Ne] $3s^2\ 3p^4$ (iii) [Ne] $3s^2\ 3p^3$

Sol.

a. $\Delta_{eg}H^{\ominus}$ of C > Si (more negative), due to small size of C than Si. [Since they contain only $4e^-$'s in the outermost shell so electron repulsion in these atoms are not very large and therefore are not considered.]

b. $\Delta_{eg}H^{\ominus}$ of Cl > F (more negative). Because adding an electron to the larger 3*p*-orbitals of Cl leads to lesser interelectronic repulsion than adding an electron to smaller 2*p*-orbitals of F.

c. $\Delta_{eg}H^{\ominus}$ of O > N

Note: $\Delta_{eg}H^{\ominus}$ of O is highly negative, while that of N is slightly positive.

Since N is quite stable due to half-filled 2*p*-orbitals, therefore it is difficult to add an extra electron to N and thus energy is required to add an extra electron.

Whereas O atom has smaller size and higher nuclear charge than N and therefore it has a high tendency to accept an extra electron. Thus energy is released.

d. $\Delta_{eg}H^{\ominus}$ of S > O [Same explanation as in part (b) above].

e. $\Delta_{eg}H^{\ominus}$ of $\dfrac{\text{Cl} > \text{F}}{\text{Group 17}} > \dfrac{\text{S}}{\text{Group 16}} > \dfrac{\text{P}}{\text{Group 15}}$

$\Delta_{eg}H^{\ominus}$ of Cl > F [as explained in part (b) above]

$\Delta_{eg}H^\ominus$ becomes more and more negative along the period ($\rightarrow$).

$\therefore \Delta_{eg}H^\ominus$ of S > P

f. Electronic configuration of (i) corresponds to Cl ($Z = 17$).
Electronic configuration of (ii) corresponds to S ($Z = 16$).
Electronic configuration of (iii) corresponds to P ($Z = 15$).
All of them belong to the 3rd period and $\Delta_{eg}H^\ominus$ becomes more and more negative along the period ($\rightarrow$).

$\therefore \Delta_{eg}H^\ominus$ of Cl > S > P

Cl contains one electron less than the stable inert gas configuration, i.e. [Ne] $3s^2\ 3p^6$ and hence has a strong tendency to accept an electron to acquire the stable inert gas configuration so the highest energy is released (more negative value).

EXAMPLE 1.9

a. The EN of cesium (Cs) is 0.7 and that of chlorine (Cl) is 3.5. Predict the bond formed between them.

b. The X–X bond length is 100pm and C–C bond length is 154pm. If EN of 'X' and 'C' are 3.0 and 2.0 respectively, calculate the C–X bond length.

i. 127pm ii. 118pm
iii. 108pm iv. 128pm

c. Which of the properties can be predicted by EN values?

d. If a, b and c are EN, IE and EA respectively. What is the formula of EA (c) in the terms of EN (a) and IE (b)?

Sol.

a. EN difference between Cs and Cl = (3.5 – 0.7) = 2.8 Thus the bond between the two is ionic or electrovalent since $(\chi_{Cs}-\chi_{Cl}) > 1.7$

b. ii. Atomic radius of X = $\dfrac{\text{Bond length}}{2} = \dfrac{100}{2} = 50\text{pm}$

Atomic radius of C = $\dfrac{\text{Bond length}}{2} = \dfrac{154}{2} = 77\text{pm}$ C–X bond length = 50 + 77 = 127pm

As there is EN difference ($\chi_x - \chi_c = 3.0 - 2.0 = 1.0$), the extent of overlapping of orbitals will be more.

Therefore, the bond length will be slightly less than 127 pm i.e. 118 pm.

c. i. Bond energy of a molecule
ii. Polarity of a molecule
iii. Nature of an oxide.
iv. Metallic and non-metallic character of elements.
v. Percentage of ionic or covalent character of a molecule.

d. EN = a, IE = b, EA = c

$$\text{EN} = \frac{\text{IE} + \text{EA}}{2} \Rightarrow \text{EA} = 2\text{EN} - \text{IE}$$

$$\Rightarrow c = 2a - b$$

EXAMPLE 1.10

Among the elements with $Z = 9$, 12 and 36, identify by atomic number of an element which is

a. Highly electropositive
b. Highly EN
c. An inert gas

Sol.

a. $Z = 12$ (Mg)
b. $Z = 9$ (F)
c. $Z = 36$ (Kr)

EXAMPLE 1.11

Explain the following questions (based on ionisation energy):

a. Why IE_1 of N is higher than that of O atom?
b. Why IE_1 of Mg is higher than that of Al atom?
c. Why IE_1 of C is greater than that of B atom whereas IE_2 is reverse?
d. In general, IE increases along the period ($\rightarrow$). Explain why the IE_2 of Cr is higher than that of Mn (Manganese)?
e. The IE_1 and IE_2 of K are 420 and 3050 kJ mol^{-1} respectively and those of Ca are 560 and 1140 kJ mol^{-1} respectively. Compare their values and comment on the differences.
f. The IE of Li, Be and C are 5.5, 9.3 and 11.3 eV. What would be the IE's of B and N?
g. Arrange the species in each group in the order of decreasing IP in each case and explain.

i. K, Ca, Sc ii. N, O, F
iii. $K^\oplus$, Ar, $Cl^\ominus$ iv. Fe, Fe^{2+}, Fe^{3+}
v. C, N, O vi. Cu, Ag, Au
vii. K, Rb, Cs viii. Be, B, C
ix. Na, Mg, Al

h. Explain why Fe^{2+} is more easily oxidised to Fe^{3+} than Mn^{2+} to Mn^{3+}.
i. Explain whether IE_1 of two isotopes of the same element would be same or different.
j. What are the factors on which IE of main group elements tends to decrease down the group ($\downarrow$).

Sol.

a. N has half-filled configuration, hence stable. Therefore IE_1 of N > IE_1 of O.

b. This is due to penetration effect. It is difficult to remove on electron from $3s$ orbital in comparison to $3p$ orbital. Hence IE_1 of Mg > IE_1 of Al.

c. Refer to Illustration 1.36.

d. Valence electronic configuration of Cr = $3d^5 4s^1$ and that of $Cr^\oplus$ is $3d^5\ 4s^0$ (stable half-filled configuration).
Valence electronic configuration of Mn = $3d^5\ 4s^2$ and that of $Mn^\oplus$ is $3d^5\ 4s^1$ (less stable configuration than that of $Cr^\oplus$).
$\therefore$ IE_2 of Cr > IE_2 of Mn

e. Valence electronic configuration of K = $4s^1$.
Valence electronic configuration of Ca = $4s^2$.

Therefore, the removal of the second electron from K is extremly difficult because K acquires noble gas configuration after the removal of one electron while the removal of both electrons from Ca is comparatively easy, as it requires stable configuration after the removal of the second electron.

f.

Group	1	2	13	14	15
2nd period	Li	Be	B	C	N

Generally IE increases along the period (→). But there is an exception in IE_1 of Be and B (due to penetration effect). Therefore, IE_1 of B should be greater than that of Be. But actually, IE_1 of Be > IE_1 of B.

Therefore, IE_1 of N (half-filled configuration) > IE_1 of C > IE_1 of Be > IE_1 of B > IE_1 of Li

g. i. Sc > Ca > K (IE of 3*d* block > group 2 > group 1).

ii. F > N > O [IE of group 17 > group 15 (half-filled configuration) > group 16]

iii. $K^{\oplus}$ > Ar > $Cl^{\ominus}$ [IE of group 1 (+ve charge) > Inert gas > group 17 (–ve charge)]

iv. $Fe^{3+} > Fe^{2+} > Fe$ [IE of +3 charge > + 2 charge > neutral element]

Valence electronic configuration of Fe, Fe^{2+} and Fe^{3+} are $3d^6\,4s^2$, $3d^6\,4s^0$ and $3d^5\,4s^0$ respectively.

v. N > O > C [IE of half filled configuration of N of group 15 > IE of group 16 > IE of group 14]

vi. Au > Cu > Ag.

5*d* > 3*d* > 4*d*

[IE should decrease from 3*d* → 4*d* → 5*d* (3*d* > 4*d* > 5*d*) transition element series. But due to imperfect screening effect of 4*f* orbitals in 5*d* transition series, the IE of 5*d* > 3*d* > 4*d*.]

vii. K > Rb > Cs [IE of group 1 decreases down the group (↓)]

viii. C > Be > B

Group ⇒ 14 2 13

[Generally IE increases along the period, i.e. from group 2 < group 13 < group 14. But there is exception in the IE of Be and B due to penetration effect, therefore, IE_1 of Be > IE_1 of B]

ix. Al > Mg > Na

[IE of group 13 > group 2 > group 1]

h. Valence electronic configuration of Fe and Fe^{2+} are $3d^6\,4s^2$ and $3d^6\,4s^0$ respectively.

Valence electronic configuration of Mn and Mn^{2+} are $3d^5\,4s^2$ and $3d^5\,4s^0$ respectively.

$$\therefore \underset{\substack{(3d^6 4s^0)\\ \text{(Less stable configuration)}}}{Fe^{2+}} \longrightarrow \underset{\substack{(3d^5,\text{ half-filled more stable}\\ \text{configuration)}}}{Fe^{3+}} + e^-$$

$$\underset{\substack{(3d^5 4s^0)\\ \text{[Half-filled more stable configuration]}}}{Mn^{2+}} \longrightarrow \underset{[3d^4,\text{ less stable configuration}]}{Mn^{3+} + e^-}$$

Fe^{2+} is easily oxidised to Fe^{3+}, since valence electronic configuration changes from less stable $3d^6$ configuration to more stable half-filled $3d^5$ configuration, whereas it is reverse in the case of Mn^{2+} to Mn^{3+}.

i. Same, since the number of protons and electrons are same but neutrons are different in isotopes of same element. Therefore, Z_{eff} and size remains same in the isotopes. Neutrons have no effect on Z_{eff} and size of isotopes.

j. i. Increase in size.

ii. Increase in screening effect.

iii. Decrease in Z_{eff}.

EXAMPLE 1.12

Answer the following questions (Based on EA, $\Delta_{eg}H^{\ominus}$ and IE).

a. IE_1 of Li is 5.4 eV atom^{-1} and the EA of Cl is 3.6 eV atom^{-1}. Calculate $\Delta_rH^{\ominus}$ in kcal mol^{-1} and kJ mol^{-1} for the reaction

$Li_{(g)} + Cl_{(g)} \longrightarrow Li^{\oplus}_{(g)} + Cl^{\ominus}_{(g)}$

formed at such a low pressure that resulting ions do not combine with each other.

b. The IE of atoms X and Y are 400 and 300 kcal mol^{-1} respectively. EA's of these atoms are 80.0 and 85.0 K cal mol^{-1}. Explain as which of the atoms has higher EN.

c. Explain why EA of S is –200 kJ mol^{-1} but the second EA is + 649 kJ mol^{-1}?

d. Which of the following pairs of elements would have more negative electron gain enthalpy ($\Delta_{eg}H^{\ominus}$)?

i. F or Cl   ii. O or F

e. What would be the second electron gain enthalpy ($\Delta_{eg}H_2^{\ominus}$) of oxygen as positive, more negative or less negative than the first ($\Delta_{eg}H_1^{\ominus}$)? Explain.

f. Which has less negative $\Delta_{eg}H^{\ominus}$ oxygen or sulphur?

Sol.

a. $Li_{(g)} \longrightarrow Li^{\oplus}_{(g)} + e^-$, $IE_1 = 5.4$ eV atom^{-1} ...(i)

$Cl_{(g)} + e^- \longrightarrow Cl^{\ominus}_{(g)}$, $EA_1 = -3.6$ eV atom^{-1} ...(ii)

Note: EA_1 is negative.

Adding Eqs. (i) and (ii), we get

$Li_{(g)} + Cl_{(g)} \longrightarrow Li^{\oplus}_{(g)} + Cl^{\ominus}_{(g)}$

$\therefore \Delta_rH^{\ominus} = IE_1 + EA_1 = 5.4 + (-3.6) = 1.8$ eV atom^{-1}

We know 1 eV atom^{-1} = 23.06 kcal mol^{-1} and 1 eV atom^{-1} = 96.49 kJ mol^{-1}

$\therefore \Delta_rH^{\ominus}$ (in kJ mol^{-1}) = 1.8 × 23.06

= 41.508 kJ mol^{-1}

$\therefore \Delta_rH^{\ominus}$ (in kcal mol^{-1}) = 1.8 × 96.49

= 173.682 kcal mol^{-1}

b. EN of $X = \dfrac{IE + EA}{125}$ (when IE and EA values are in kcal mol^{-1})

$= \dfrac{400 + 80}{125} = 3.84$

$$\text{EN of } Y = \frac{300 + 85}{125} = 3.08$$

$\therefore$ EN of $X >$ EN of Y

c. $S_{(g)} + e^- \longrightarrow S^{\ominus}_{(g)}$, $EA_1 = -200$ kJ mol^{-1}

$S^{\ominus}_{(g)} + e^- \longrightarrow S^{2-}_{(g)}$, $EA_2 = +649$ kJ mol^{-1}

The addition of the second electron to $S^{\ominus}(g)$ experience repulsion from the already present electrons.

d. i. Cl. When electron is added to F, the added electron goes to smaller $n = 2$ (i.e. $2p$ orbital) quantum level and suffers significant repulsion from the other electrons present in that shell. So, electron is being added with difficulty in F than in Cl. Hence less negative energy in released in F than in Cl. So, $\Delta_{eg}H^{\ominus}$ of F is less negative than Cl.

ii. F. $\Delta_{eg}H^{\ominus}$ of F is more negative then O due to the small size of F than O. Moreover, $\Delta_{eg}H^{\ominus}$ increases (more negative) along the period ($\rightarrow$).

e. $e^- + O_{(g)} \longrightarrow O^{\ominus}_{(g)}$ $EA_1 = -200$ kJ mol^{-1}

$e^- + O^{\ominus}_{(g)} \longrightarrow O^{2-}_{(g)}$, $EA_2 = ?$

EA_2 is positive due to more electron–electron repulsion.

f. Due to the compact nature of oxygen atom it has less negative $\Delta_{eg}H^{\ominus}$ (–141 kJ mol^{-1}) than S(–200 kJ mol^{-1}). [Same explanation as in $\Delta_{eg}H^{\ominus}$ of F and Cl, refer to the above part (d) (i).]

EXAMPLE 1.13

Explain the following questions (based on size of atoms or ions and other periodic properties):

a. Arrange the following species in decreasing order of their sizes/ionic radii.

i. Ar, $K^{\oplus}$, $Cl^{\ominus}$, S^{2-} and Ca^{2+}

ii. Al^{3+}, Mg^{2+}, $Na^{\oplus}$, $Cl^{\ominus}$, N^{3-} and O^{2-}

b. What are isoelectronic species? Name the species which are isoelectronic with each of the following atoms or ions.

i. $Rb^{\oplus}$ ii. $F^{\ominus}$ iii. Mg^{2+} iv. Ar

c. Arrange the following species/atoms in decreasing order of reducing character.

i. Na, Mg and Al ii. Mg, Ca and Sr

iii. Na, K and Rb iv. $F^{\ominus}$, $Cl^{\ominus}$, $Br^{\ominus}$ and $I^{\ominus}$

d. The decreasing order of reactivity of group 1 elements is Cs > Rb > K > Na > Li whereas that of group 17 elements is (Cl > F > Br > I). Explain.

e. Predict the formula of the stable binary compounds that would be formed by the combination of the following pairs of elements:

i. Mg and N

ii. Si and O

iii. Element with $Z = 71$ and F

iv. P and F

v. Al and I

vi. Li and O

f. Answer the following by the use of periodic table.

i. Identify the element that would tend to gain two electrons.

ii. Identify the group having metal, non-metal, liquid as well as gas at the room temperature.

iii. Identify the element with five electrons in the outer shell.

iv. Identify the element that would tend to lose two electrons.

Sol.

a. i. All of them are isoelectronic species, with 18 electrons.

$\therefore$ Size of more negative ion > size of inert gas > size of less positive > size of more positive ion.

$\therefore$ $S^{2-} > Cl^{\ominus} > Ar > K^{\oplus} > Ca^{2+}$

ii. $N^{3-} > O^{2-} > F^{\ominus} > Na^{\oplus} > Mg^{2+} > Al^{3+}$

(All of them are isoelectronic species with 10 electrons)

b. Isoelectronic species have same number of electrons.

i. $Rb^{\oplus}$ ($Z = 37$, No. of e^-'s $= 37 - 1 = 36$) is isoelectronic with Sr^{2+} ($Z = 38$, No. of e^-'s $= 38 - 2 = 36$).

ii. $F^{\ominus}$ ($Z = 9$, No. of e^-'s $= 9 + 1 = 10$) is isoelectronic with Ne ($Z = 10$).

iii. Mg^{2+} ($Z = 12$, No. of e^-'s $= 12 - 2 = 10$) is isoelectronic with $Na^{\oplus}$ ($Z = 11$, No. of e^-'s $= 11 - 1 = 10$) and with Ne ($Z = 10$).

iv. Ar ($Z = 18$), is isoelectronic with Ca^{2+} ($Z = 20$, No. of e^-'s $20 - 2 = 18$).

c. Elements with low IE and large size have more tendency to undergo oxidation and thus acts as stronger reducing agent.

i. Na (group 1) > Mg (group 2) > Al (group 13 elements). [IE increases along the period ($\rightarrow$). All of them belong to the 3rd period].

ii. Sr > Ca > Mg [All of them belong to group 2 and IE decreases down the group ($\downarrow$)].

iii. Rb > K > Na [Group 1 elements. IE decreases down the group ($\downarrow$).]

iv. $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$ [Group 17, size increases and IE decreases down the group ($\downarrow$).]

d. The reactivity of group 1 element is the tendency to lose electrons easily, i.e., to undergo oxidation easily. Low IE and large size of group 1 elements, so more reactive is the element. Hence reactivity order of group 1 elements is Cs > Rb > K > Na > Li [IE decreases down the group ($\downarrow$)]

The reactivity of group 17 element is the tendency to accept electrons easily, i.e. to undergo reduction easily. High is the negative EA or $\Delta_{eg}H^{\ominus}$ of group 17 elements so more reactive is that element (or magnitude of EA or $\Delta_{eg}H^{\ominus}$ decreases down the group except in case of F and Cl).

Therefore, reactivity order of group 17 elements is Cl > F > Br > I ($\Delta_{eg}H^{\ominus} = -349 > -333 > -325 > -296$ kJ mol^{-1})

e. i. Mg^{2+} and N^{3-} give Mg_3N_2 (Magnesium nitride)

ii. Si^{4+} and O^{2-} give $Si_2O_4 \Rightarrow SiO_2$ (Silicon dioxide)

iii. Element with $Z = 71$ is lutetium (Lu) and general oxidation states (OS) of lanthanides and actinides is +3.

So Lu^{3+} and $F^{\ominus}$ give LuF_3 (Lutetium trithoride)

iv. P^{5+} and $F^{\ominus}$ give PF_5 (Phosphorous pentafluoride)

v. Al^{3+} and $I^{\ominus}$ give AlI_3 (Aluminium triiodide)

vi. $Li^{\oplus}$ and O^{2-} give Li_2O (Lithium monoxide)

f. i. Only oxygen atom in group 16 has OS of –2 (except in case of peroxides and OF_2).

The other element of group 16 (e.g. S, Se, Te, Po), besides –2 OS, they also show +2, +4 and +6 OS.

So, oxygen tends to gain two electrons to attain noble gas stable configuration.

ii. Group 17 elements Metal is At (Astatine), non-metal is Cl (Chlorine), liquid is Br_2 (Bromine) and gas is F_2 and Cl_2.

iii. Group 15 elements. The valence electronic configuration of N is $2s^22p^3$.

iv. Group 2 elements, e.g. $Mg \rightarrow Mg^{2+}(g) + 2e^-$

EXAMPLE 1.14

For the gaseous reaction

$$K + F \longrightarrow K^{\oplus} + F^{\ominus}$$

$\Delta H = 19\ \text{kcal mol}^{-1}$ under the conditions when cations and anions are prevented by electrostatic separation from combining with each other. The IE_1 of K is 4.3 eV. Calculate $\Delta_{eg}H^{\ominus}$ of F.

Sol. $K_{(g)} \longrightarrow K^{\oplus}_{(g)} + e^-$ $\quad IE_1 = 4.3\ \text{eV atom}^{-1}$ ...(i)

$e^- + F_{(g)} \longrightarrow F^{\ominus}_{(g)}$ $\quad$ Let $\Delta_{eg}H_1^{\ominus} = y\ \text{eV atom}^{-1}$ ...(ii)

Adding Eqs. (i) and (ii), we get

$K_{(g)} + F_{(g)} \longrightarrow K^{\oplus}_{(g)} + F^{\ominus}_{(g)}$

$\therefore IE_1 + \Delta_{eg}H_1^{\ominus} = 19\ \text{kcal mol}^{-1} = 0.82\ \text{eV atom}^{-1}$ ...(iii)

Note: Use direct relation: $1\ \text{eV} = 23.06\ \text{kcal mol}^{-1}$

$$\therefore 19\ \text{kcal mol}^{-1} = \frac{19.0}{23.06} = 0.82\ \text{eV atom}^{-1}$$

Alternatively:

Convert 19 kcal mol^{-1} in eV atom^{-1} as follows: ($1\ \text{eV} = 1.6 \times 10^{-10}$ J)

$$19\ \text{kcal mol}^{-1} = 19 \times 10^3\ \text{cal mol}^{-1}$$
$$= 19 \times 10^3 \times 4.18\ \text{J mol}^{-1}$$
$$= \frac{19 \times 10^3 \times 4.18}{1.6 \times 10^{-19}}\ \text{eV mol}^{-1}$$
$$= \frac{19 \times 10^3 \times 4.18}{1.6 \times 10^{-19}} \times \frac{1}{6.023 \times 10^{23}}\ \text{eV atom}^{-1}$$
$$= 0.82\ \text{eV atom}^{-1}$$

Substituting the value of IE_1 in Eq. (iii), we get

$4.3\ \text{eV atom}^{-1} + \Delta_{eg}H_1^{\ominus} = 0.82\ \text{eV atom}^{-1}$

$\therefore \Delta_{eg}H_1^{\ominus} = (0.82 - 4.3) = -3.48\ \text{eV atom}^{-1}$

EXAMPLE 1.15

For the reaction

$K_{(g)} + F_{(g)} \rightarrow K^{\oplus} + F^{\ominus}$ (separated ions, $\Delta H = 19\ \text{kcal mol}^{-1}$)

If the IE_1 of K and $\Delta_{eg}H_1^{\ominus}$ of $F^{\ominus}$ have a geometric mean of 3.88 eV and $IE_1 > \Delta_{eg}H_1^{\ominus}$. Calculate the value of IE_1 and $\Delta_{eg}H_1^{\ominus}$.

Given: $19\ \text{kcal mol}^{-1} = 0.82\ \text{eV atom}^{-1}$ (as in Example 1.14 above)

Sol. $K_{(g)} \longrightarrow K^{\oplus}_{(g)} + e^-$; $IE = x\ \text{kcal mol}^{-1}$ ...(i)

$F_{(g)} + e^- \longrightarrow F^{\ominus}_{(g)}$; $\Delta_{eg}H^{\ominus} = -y\ \text{kcal mol}^{-1}$ ...(ii)

Adding Eqs. (i) and (ii), we get

$K_{(g)} + F_{(g)} \longrightarrow K^{\oplus}_{(g)} + F^{\ominus}_{(g)}$

$\therefore x - y = 19\ \text{kcal mol}^{-1} = 0.82\ \text{eV}$ ...(iii)

$\sqrt{xy} = 3.88\ \text{eV} \Rightarrow xy = (3.88)^2 = 15.0544$

$$\therefore x = \frac{15.0544}{y}$$

Substituting the value of x in Eq. (iii), we get

$$\frac{15.0544}{y} - y = 19$$

Solving, we get

$y = 3.48$ eV

$x + y = 7.48$ eV ; $\quad x - y = 0.82$ eV

$\therefore IE = x = 4.313$ eV

$\Delta_{eg}H^{\ominus} = -y = -3.48$ eV

EXAMPLE 1.16

From N atoms of an element A, when half the atoms transfer one electron to the another atom. 405 kJ mol^{-1} of energy was found to be consumed. An additional energy of 745 kJ mol^{-1} was further required to convert all the $A^{\ominus}$ ions to $A^{\oplus}$. Calculate the ionisation energy and the electron gain enthalpy of atom A in eV (1 eV = 96.48 kJ).

Sol. $N/2(A \longrightarrow A^{\oplus} + e^-)$; IE = +ve

$N/2(A + e^- \longrightarrow A^{\ominus})$; $\Delta_{eg}H^{\ominus}$ –ve

Let x and y are the IE and $\Delta_{eg}H^{\ominus}$ respectively.

$$\therefore \frac{1}{2}(x - y) = 405\ \text{kJ}$$
$$\frac{1}{2}(x + y) = 745\ \text{kJ}$$

On solving $x = 1150$ and $y = 340$ kJ

or $\quad$ 1150 kJ= 11.91 eV

Similarly, 340 kJ = 3.52 eV

IE = 11.9 eV and $\Delta_{eg}H^{\ominus} = -3.5$ eV

EXAMPLE 1.17

The conversion of gaseous atoms K and F to $K^{\oplus}$ and $F^{\ominus}$ absorbs 0.85 eV of energy. If the IE and $\Delta_{eg}H^{\ominus}$ of K and F have magnitudes in the ratio of 7 : 6, what is the electron gain enthalpy ($\Delta_{eg}H^{\ominus}$) of fluorine?

Sol. $K_{(g)} \longrightarrow K^{\oplus}_{(g)} + e^-$; IE $= x$ eV atom^{-1} ...(i)

$F_{(g)} + e^- \longrightarrow F^{\ominus}_{(g)}$; $\Delta_{eg}H^{\ominus} = -y$ eV ...(ii)

$K_{(g)} + F_{(g)} \longrightarrow K^{\oplus}_{(g)} + F^{\ominus}_{(g)}$

$\therefore$ IE $+ \Delta_{eg}H^{\ominus} = x + (-y) = 0.85$ eV atom^{-1} ...(iii)

Given: $\frac{x}{y} = \frac{7}{6}$ ...(iv)

From Eqs. (iii) and (iv), solve for x and y,

$y = 5.10$ eV atom^{-1}

$\therefore \Delta_{eg}H^{\ominus} = -y = -5.10$ eV atom^{-1}

EXAMPLE 1.18

Explain the following:

a. Which of the elements Na, Mg, Si and P would have the greatest difference between the IE_1 and IE_2? Explain?

b. The EN's of B, Al and Ga are 2.0, 1.5 and 1.6 respectively. The trend is not regular. Explain?

c. Li_2CO_3 decomposes on heating but other alkali metal carbonate (e.g. Na_2CO_3) does not. Explain?

d. Explain why $Cu^{\oplus}$ is found only is solid state and not in solutions.

e. Be of N have extremely low value of EA (i.e. less negative value) against the trend. Explain?

f. Arrange the following in decreasing order of their properties indicated:

$Na^{\oplus}$ Mg^{2+} and Al^{3+}

i. Ionic mobility in H_2O

ii. Size of ions

iii. Standard reduction potential ($E^{\ominus}_{M^{x+}(aq)}/M_s$)

iv. Extent of hydration

v. Hydration energy

vi. Size of hydrated ions

g. In iodometry, why KI is not added dropwise to an acidified solution of $KMnO_4$ but reverse is done?

h. Why the decrease in size between Li and Be is much greater than that between Na and Mg or K and Ca?

i. K_2CO_3 is less soluble than Cs_2CO_3 or Rb_2CO_3 while among group 2 elements $MgCO_3$ is more soluble than $BaCO_3$.

j. Explain the decreasing order of solubility of sulphate of group 2 element.

k. 'EA of Cl is the highest among the halogens, yet F is the strongest oxidising agent'. Why?

Sol.

a. Elements having stable noble gas configuration after removal of one electron will have the maximum difference between IE_1 and IE_2 so the element is Na.

Electronic configuration of Na, $Na^{\oplus}$ and Na^{2+} ion

$$Na = 1s^2, 2s^2\,2p^6, 3s^1 \xrightarrow[\text{from } 3s]{-e^-} Na^{\oplus}\,(1s^2, 2s^2\,2p^6)$$

$$\downarrow -e^- \text{ from } 2p$$

$$Na^{2+}\,(1s^2, 2s^2\,2p^5)$$

A jump in IE is noticed only when the valence shell changes during the successive removal of electrons.

b. B, Al and Ga belong to group 13, and down the group (↓), EN decreases. But after Al, due to the imperfect (minimum) shielding effect of *d* electrons, the nuclear charge increases and hence EN also increases.

Group 13	EN
B	2.0
Al	1.5
Ga	1.6
In	1.7
Tl	1.8

c. Comparable sizes of the ions form the strongest lattice, so crystal lattice of Li_2CO_3 is not so strong due to small size of $Li^{\oplus}$ and larger size of CO_3^{2-}. So Li_2CO_3 decomposes on heating. But other alkali metal carbonates (e.g. Na_2CO_3), have strong crystal lattice, due to comparable size of cation (e.g. $Na^{\oplus}$ ion and CO_3^{2-} ion). So they are stable to heat.

$$\left.\begin{array}{l} Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2 \\ MgCO_3 \xrightarrow{\Delta} MgO + CO_2 \end{array}\right] \text{Due to diagonal relationship of Li and Mg}$$

Na_2CO_3, K_2CO_3 etc. $\xrightarrow{\Delta}$ No action

Note: The crystal lattice of Li_2O is stronger due to comparable sizes of $Li^{\oplus}$ and O^{2-} ions.

d. In solution $Cu^{\oplus}$ disproportionate to Cu^{2+} and Cu, but in solid state it does not. So, $Cu^{\oplus}$ ion is found only in solid state.

$$2Cu^{\oplus}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + Cu \qquad \Delta_rG^{\ominus} = -ve$$

e. Valence electronic configuration of Be and N:

$Be = 2s^2\,2p^0$, $\quad N = 2s^2\,sp^3$

In Be, the incoming electron has to be added in $2p$ orbitals because $2s$ orbital is completely filled and in N, it is to be added to half-filled $2p$ orbitals. Since half-filled and full-filled orbitals are more stable, therefore incoming electron will be added with difficulty. Hence Be and N have low value of EA (i.e. less negative value).

f. i. Hydration energy or extent of hydration increases along the period (→). Greater the extent of hydrations, lesser is the ionic mobility in aqueous solution:

$\therefore Na^{\oplus} > Mg^{2+} > Al^{3+}$

ii. The greater the positive charge, the lesser is the size,

$\therefore Na^{\oplus} > Mg^{2+} > Al^{3+}$

iii. The greater the positive charge, the higher is the reduction potential value.

$\therefore E^{\ominus}_{Al^{3+}(aq)/Al_{(s)}} > E^{\ominus}_{Mg^{2+}(aq)/Mg_{(s)}} > E^{\ominus}_{Na^{\oplus}(aq)/Na_{(s)}}$

iv. Extent of hydration increases along the period due to increase in charge density $\left(\frac{\text{charge}}{\text{size}} \text{ ratio}\right)$

$\therefore Al^{3+} > Mg^{2+} > Na^{\oplus}$

v. Same explanation as in part (iv) above

The greater the extent of hydration the more (negative) energy is released

$\therefore Al^{3+} > Mg^{2+} > Na^{\oplus}$

vi. The greater the extent of hydration, the larger is the size of that ion (reverse of the size of ions).

$\therefore Al^{3+} > Mg^{2+} > Na^{\oplus}$

g. Iodometry: The estimation of oxidising substance involving the liberation of I_2 and subsequent volumetric estimation of I_2 is called iodometry, e.g.

$2\,Cu^{2+} + 4\,I^{\ominus} \longrightarrow Cu\,I_2 + I_2$

$2\,Cu\,I_2 \longrightarrow Cu_2\,I_2 + I_2$

If KI is added dropwise to acidic $KMnO_4$ solution, then $MnO_4^{\ominus}$ will oxidise $I^{\ominus}$ to $IO_3^{\ominus}$ and $IO_4^{\ominus}$ instead of I_2.

> **Note:** Iodometry is the estimation of reducing substance by use of standard I_2, e.g.
> $I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^{\ominus}$

h. From Li ($2s^1$) to Be ($2s^2$), the additional electron is added to the $2s$ orbital or (L shell) which is quite closer to nucleus whose charge is also increased by 1 unit. So, greater force is experienced by the electron and size decreases.

From Na ($3s^1$) to Mg ($3s^2$) and K ($4s^1$) to Ca ($4s^2$), the electrons are added in $3s$ and $4s$ orbitals (or M and N shell) respectively, which are away from nucleus. So, lesser force of attraction is experienced by the electrons and decrease in size is less than that of decrease in size between Li and Be. Moreover, screening effect also contributes in the small decreases in the sizes of Na and K and K and Ca.

i. K_2CO_3 is less soluble than Cs_2CO_3 or Rb_2CO_3 because IE factor out weighs hydration energy factor (K has high IE and high hydration energy and Cs and Rb have low IE and low hydration energy).

But it is reverse for group 2 element carbonates (refer to Section 1.27.1, Point 10(c).

j. For explanation, refer to Section 1.27.1, Point 10(c).

k. EA of Cl is more negative (-349 kJ mol^{-1}) than that of F (-333 kJ mol^{-1}). But the reduction potential value or oxidising ability of F_2

(i.e. $E^{\ominus}_{\frac{1}{2}F_2(g)/F^{\ominus}(aq)} = 2.87$ V)

is greater than that of Cl_2

(i.e. $E^{\ominus}_{\frac{1}{2}Cl_2(g)/Cl^{\ominus}(aq)} = 1.36$ V)

as shown by Born–Haber cycle.

i.

$$\frac{1}{2}F_{2(g)} \xrightarrow{\frac{1}{2}\Delta_{diss}H^{\ominus} = \frac{160}{2} = 80\ kJ\,mol^{-1}} F_{(g)} + e^- \xrightarrow{EA = -333\ kJ\,mol^{-1}} F^{\ominus}_{(g)} + aq \xrightarrow{\Delta_{hyd}H^{\ominus} = -515\ kJ\,mol^{-1}} F^{\ominus}_{(aq)}$$

$\therefore\ \Delta_r H^{\ominus}\ (80 - 333 - 515) = -768$ kJ mol^{-1}.

> **Note:** $\Delta_{diss}H^{\ominus}$ of $Cl_{2(g)} > Br_{2(g)} > F_{2(g)} > I_{2(g)}$

ii.

$$\frac{1}{2}Cl_{2(g)} \xrightarrow{\frac{1}{2}\Delta_{diss}H^{\ominus} = \frac{242}{2} = 121\ kJ\,mol^{-1}} Cl_{(g)} + e^- \xrightarrow{EA = -349\ kJ\,mol^{-1}} Cl^{\ominus}_{(g)} + aq \xrightarrow{\Delta_{hyd}H^{\ominus} = -422\ kJ\,mol^{-1}} Cl^{\ominus}_{(aq)}$$

$\therefore\ \Delta_r H^{\ominus}\ (121 - 349 - 422) = -650$ kJ mol^{-1}

F has low $\Delta_{diss}H^{\ominus}$, high (negative) $\Delta_{hyd}H^{\ominus}$ and less negative EA than that of Cl. Thus overall position is that F has the largest negative $\Delta_r H^{\ominus}$ value (i.e. -768 kJ mol^{-1}) than that of Cl (i.e. -650 kJ mol^{-1}).

So, reaction $\left(\frac{1}{2}F_{2(g)} \text{ to } F^{\ominus}_{(aq)}\right)$ is more feasible than that of $\left(\frac{1}{2}Cl_{2(g)} \text{ to } Cl^{\ominus}_{(aq)}\right)$. Therefore, the more is the negative $\Delta_r H^{\ominus}$ value of a reaction the more positive will be its reduction potential value. Hence, F is the strongest oxidising agent among halogens.

EXAMPLE 1.19

Classify the following oxides as

a. Strongly acidic **b.** Weakly acidic
c. Neutral **d.** Amphoteric
e. Weakly basic and **f.** Strongly basic

i. SnO_2	ii. SnO	iii. CO	iv. PbO
v. MnO_2	vi. RaO	vii. N_2O	viii. FeO
ix. Ag_2O	x. OsO_4	xi. Al_2O_3	xii. Fe_2O_3
xiii. CeO_2	xiv. CO_2	xv. MgO	xvi. K_2O

Sol.

Strongly acidic	Weakly acidic	Neutral	Amphoteric	Weakly basic	Strongly basic
None	(x) OsO_4 Weakly acidic as expected for such high oxidation state (xiv) CO_2	(iii) CO (v) MnO_2 (vii) N_2O	(i) SnO_2 (ii) SnO (xi) Al_2O_3	(iv) PbO (viii) FeO (xii) Fe_2O_3	(vi) RaO (ix) Ag_2O (xiii) CeO_2 (xv) Moderately strongly basic MgO (xvi) K_2O

EXAMPLE 1.20

Select the strongest and weakest acid in each of the following sets:

a. HBr, HF, H_2Te, H_2Se, PH_3, H_2O

b. HClO, HIO, H_3PO_3, H_2SO_3, H_3AsO_3

Sol.

a. HBr, a strong acid, is the strongest in the given set.

PH_3, which has weakly basic properties, is least acidic.

b. H_2SO_3, which is farthest to the right in the periodic table and has the most oxygen atoms, is the most acidic.

$HClO$, with the fewest oxygen atoms and the farthest up in the periodic table, is the weakest.

EXAMPLE 1.21

A 0.10 M aqueous solution of which salt in each of the following pairs would have the higher pH?

a. $NaNO_2$ or $NaAsO_2$ b. NaF or Na CN

c. Na_2SO_3 or Na_2TeO_3 d. NaOCl or NaOBr

Sol. The stronger the acid, the weaker is its conjugate base. The oxyacids are stronger towards the top of the periodic table.

a. HNO_2 is a stronger acid; hence, $NO_2^{\ominus}$ is a weaker base. Therefore, $AsO_2^{\ominus}$ has a higher pH (Note: Higher pH means more basic, and lower pH means more acidic).

b. HF is a stronger acid; hence, $F^{\ominus}$ is a weaker base. Therefore, $CN^{\ominus}$ has a higher pH.

c. H_2SO_3 is a stronger acid; SO_3^{2-} is a weaker base; TeO_3^{2-} has a higher pH.

d. HOCl is a stronger acid; $OCl^{\ominus}$ is a weaker base; $OBr^{\ominus}$ has a higher pH.

EXAMPLE 1.22

Identify:

a. The good oxidising agent(s)

b. The good reducing agent

c. The good dehydrating agent(s)

among the following substances:

H_2SO_3, HNO_3, P_4O_{10}, H_3PO_4, H_2S, H_2SO_4.

Sol.

a. Good oxidising agents: HNO_3 and H_2SO_4 (Conc.)

b. Good reducing agent: H_2S

c. Good dehydrating agents: H_2SO_4 and P_4O_{10}

EXAMPLE 1.23

Answer the following:

a. Which of the following has the greatest affinity for water: P_4O_{10}, Cl_2O, I_2O_5.

b. Which of the following is the most basic: Al_2O_3, Tl_2O_3, Tl_2O.

c. Which of the following has the lowest melting point: LiBr, $BeBr_2$, BBr_3.

d. Which of the following has highest EN: Li, Be, Mg.

e. Which of the following is most stable towards oxidation: $GeCl_2$, $SnCl_2$, $PbCl_2$.

f. Which of the following is the strongest oxidising agent: CrO_4^{2-}, MoO_4^{2-}, WO_4^{2-}.

Sol.

a. P_4O_{10}. It is more powerful as a dehydrating agent than Cl_2O_7 since the latter is the product of dehydration of $HClO_4$ by P_4O_{10}. Reverse reaction does not proceed so well.

Since I_2O_5 can be prepared by heating HIO_3, it cannot have too great an affinity for water. In fact, P_4O_{10} is one of the most powerful dehydrating agents known.

b. Apply Fajans' rule, more ionic a compound more basic is it (large cation and less charge). So, Tl_2O is more basic. Therefore, basic or ionic order is

$$\overset{1+}{Tl_2O} > \overset{3+}{Tl_2O_3} > \overset{3+}{Al_2O_3}$$

c. Apply Fajans' rule, more covalent a compound, lesser is the melting point (small cation and high charge). So, BBr_3 is having the lowest melting point.

Covalent character order: $\overset{3+}{BBr_3} > \overset{2+}{BeBr_2} > \overset{\oplus}{LiBr}$

Melting point order: $BBr_3 < BeBr_2 < LiBr$

d. EN increases along the period, i.e. from Li to Be (2nd period) but decreases down the group. So, Be is the most EN element. Order of EN: Be (1.5) > Mg (1.2) > Li (1.0)

e. $PbCl_2$. The inert pair effect of the 6th period element is more stable than those of the 5th period elements and far more stable than the analogous pair in the 4th period.

Alternatively:

Down the group; inert pair effect is more stable.

Group 14	Stable OS
C	+4
Si	+4
Ge	+4 +2
Sn	+4 +2
Pb	– +2

Note: OS in circle is more stable.

So, Pb^{2+} is difficult to oxidise to Pb^{4+} ion

$Pb^{2+} \rightarrow Pb^{4+} + 2e^-$ (oxidation)

∴ Therefore, order of stability towards oxidation:

$PbCl_2 > SnCl_2 > GeCl_2$.

f. CrO_4^{2-}. The higher oxidation states of the 2nd and 3rd transition series elements are more stable.

Order of oxidising agent: $CrO_4^{2-} > MoO_4^{2-} > WO_4^{2-}$

Transition element series 1 2 3

EXAMPLE 1.24

Explain the following:

a. The formation of Cs_2O from its element is less exothermic than the formation of ZnO from its element.

b. On the basis of appropriate Born–Haber cycle, state what factor(s) is (are) responsible for the fact that lithium nitride (Li_3N) is more stable while potassium nitride (K_3N) is unstable.

c. Why Al^{3+} is the only stable oxidation state of Al in its compounds while Tl has +1 and +3 oxidation states?

d. Pb^{4+} is a powerful oxidising agent. What is the reducing ability of Pb^{2+}?

e. Which is more soluble in water LiI or KI?

Sol.

a. The lattice energy of ZnO must be greater since it is the major contribution to the exothermic nature of each reaction.

b. The lattice energy of Li_3N is higher than that of K_3N, due to the large difference in ionic size between $Li^{\oplus}$ and $K^{\oplus}$ ions.

Note: Comparable size of the ions forms the strongest lattice, so sizes of $Li^{\oplus}$ and N^{3-} are comparable.

The difference in IE, sublimation energy and other factors of the Born–Haber cycle are relatively small between the two compounds.

c. Tl has an inert pair of electrons ($6s^2$); Al has no corresponding inert pair.

d. Due to the inert pair effect Pb^{2+} is more stable than Pb^{4+}. Therefore, Pb^{4+} can undergo reduction easily and acts as powerful oxidising agent.

$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}$ (reduction and acts as oxidising agent)

Therefore, Pb^{2+} cannot undergo oxidation easily and hence acts as a relatively poor reducing agent.

$Pb^{2+} \longrightarrow Pb^{4+} + 2e$ [does not undergo oxidation]

e. LiI. According to Fajans' rule, LiI is less ionic than KI and therefore KI should be more soluble in H_2O than LiI.

But the lattice energy of LiI (small cation and large anion) is less than that of KI, due to comparable sizes of $K^{\oplus}$ and $I^{\ominus}$ ions. Thus the energy required to break up the lattice of LiI is lower and is easily provided by hydration energy. So, LiI is more soluble in H_2O than KI.

EXAMPLE 1.25

Give the name and atomic number of the inert gas atom in which the total number of *d*-electrons is equal to the difference in number to the total *p*- and *s*-electrons.

Sol. The first inert gas which contains *d*-electron is in 4th period (or from 3*d* transition element series), i.e. Kr ($Z = 36$).

Electronic configuration of Kr:

$1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^6$.

Total number of *d*-electrons = 10

Total number of *p*-electrons = 6 + 6 + 6 = 18

Total number of *s*-electrons = 2 + 2 + 2 + 2 = 8

Difference in total number of *p*- and *s*-electrons = (18 − 8) = 10

Thus, the inert gas is Kr (krypton).

EXAMPLE 1.26

Classify the elements having atomic numbers (9, 12, 16, 34, 53, 56) into three separate pairs on the basis of similar chemical properties.

Sol. 2nd period ends with $Z = 10$

3rd period ends with $Z = 10 + 8 = 18$

4th period ends with $Z = 18 + 18 = 36$

5th period ends with $Z = 36 + 18 = 54$

Note: Magic numbers are 8, 18, 18 and 32.

a. $Z = 9$ (10 − 1) (group 18 − 1) = group 17, 2nd period, element is F.

b. $Z = 12$ (10 + 2) (group 2), 3rd period, element is Mg.

c. $Z = 16$ (18 − 2) (group 18 − 2) = group 16, 3rd period, element is S.

d. $Z = 34$ (36 − 2) (group 18 − 2) = group 16, 4th period, element is Se.

e. $Z = 53$ (54 − 1) (group 18 − 1) = group 17, 5th period, element is I.

f. $Z = 56$ (54 + 2) (group 2), 5th period and element is Ba.

i. Therefore, elements with atomic number 9 (F) and 53 (I) belong to group 17, i.e. halogens.

ii. Elements with atomic number 12 (Mg) and 56 (Ba) belong to group 2, i.e. alkaline earth metals.

iii. Elements with atomic number 16(S) and 34 (Se) belongs to group 16, i.e. oxygen family.

EXAMPLE 1.27

Calculate the electronegativity of fluorine from the following data:

$E_{H-H} = 104.2$ kcal mol^{-1}, $E_{F-F} = 36.6$ kcal mol^{-1}

$E_{H-F} = 134.3$ kcal mol^{-1}, $\chi_H = 2.1$

Sol. Let the electronegativity of fluorine be χ_F.

Applying Pauling's equation

$$\chi_F - \chi_H = 0.208\,[E_{H-F} - (E_{F-F} \times E_{H-H})^{1/2}]^{1/2}$$

In this equation, dissociation energies are taken in kcal mol^{-1}

$$\chi_F - 2.1 = 0.208[134.6 - (104.2 \times 36.6)^{1/2}]^{1/2}$$

$$\chi_F = 3.87$$

EXAMPLE 1.28

Calculate the electronegativity of carbon from the following data:

$E_{H-H} = 104.2$ kcal mol^{-1}, $E_{C-C} = 83.1$ kcal mol^{-1}

$E_{C-H} = 98.8$ kcal mol^{-1}, $\chi_H = 2.1$

Sol. Let the electronegativity of carbon be χ_C.

Applying Pauling's equation.

$$\chi_C - \chi_H = 0.208\,[E_{C-H} - (E_{C-C} \times E_{H-H})^{1/2}]^{1/2}$$

$$\chi_C - 2.1 = 0.208\,[98.8 - (83.1 \times 104.2)^{1/2}]^{1/2}$$

$$\chi_C = 2.59$$

EXAMPLE 1.29

Ionisation potential and electron affinity of fluorine are 17.42 and 3.45 eV respectively. Calculate the electronegativity of fluorine.

Sol. According to Mulliken's equation

$$\chi = \frac{IP + EA}{5.6}$$ when both IP and EA are taken in eV

$$\chi_F = \frac{17.42 + 3.45}{5.6} = 3.726$$

EXAMPLE 1.30

Calculate the EN of silicion using Allred–Rochow method. Covalent radius of silicon is 1.75 Å.

Sol. Allred–Rochow equation is

$$\chi = 0.359 \times \frac{Z_{eff}}{r^2} + 0.744$$

(Z_{eff} is calculated on the basis of Slater's rules taking all the electrons.)

Electronic configuration of Si (Z = 14) is

$1s^2, 2s^2\, 2p^6, 3s^2\, 3p^2$

$Z_{eff} = 14 - (0.35 \times 4 + 0.85 \times 8 + 2 \times 1) = 3.80$

$$\chi = 0.359 \frac{3.80}{(1.175)^2} + 0.744 = 1.73$$

EXAMPLE 1.31

Calculate the electronegativity value of chlorine on Mulliken's scale, given that IP = 13.0 eV and EA = 4.0 eV.

Sol. $\chi_{Cl} = \frac{(IP)_{Cl} + (EA)_{Cl}}{5.6} = \frac{13+4}{5.6} = 3.03$

EXAMPLE 1.32

Find the electronegativity of lead with the help of the given values. Screening consitant (σ) of Pb = 76.70. atomic number of lead = 82 and covalent radius of Pb = 5.3 Å

Sol. Substituting the value of σ, Z and r in Allered–Rochow's scale ...(i)

$Z_{eff} = Z - \sigma = 82 - 76.70 = 5.3.$

$$\chi_{Pb} = 0.359 \times \frac{Z_{eff}}{r^2} + 0.744$$

$$= 0.359 \times \frac{5.3}{(5.3)^2} + 0.744$$

$$= 1.55$$

EXAMPLE 1.33

The ionisation potentials of atoms A and B are 400 and 300 kcal mol^{-1} respectively. The electron gain enthalpy of these atoms are 80.0 and 85.0 kcal mol^{-1} respectively. Which of the atoms has higher electronegativity.

Sol. Substituting the value of IP, EA (or $\Delta_{eg}H^{\ominus}$) in equation of Mulliken's scale, we get

$$\chi_A = \frac{400+80}{2 \times 62.5} = 3.84$$

$$\chi_B = \frac{300+85}{2 \times 62.5} = 3.08$$

Hence atom A has higher EN.

EXAMPLE 1.34

Consider the following orders and identify the correct order:

(I) Ionic radius: $Se^{2-} > S^{2-} > K^{\oplus} > Mg^{+2}$

(II) Electrical conductance in aqueous solution: $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

(III) Hydration energy: $Al^{+3} > Mg^{2+} > Li^{\oplus}$

(IV) Lewis acidic character: $SiCl_4 > AlCl_3 > BeCl_2$

(V) Lattice energy: LiF > NaF > KF > RbF

(VI) Electronegativity of central C-atom: $CF_4 > CCl_4 > CH_4$

(VII) Lewis basic character: HF > HCl > HBr > HI

(VIII) Ionisation energy: Ni > Pd > Pt

(IX) Stable oxidation state: $As^{+5} > Sb^{5+} > Bi^{5+}$

(X) Metallic character: Ge > As > Se > Br

(XI) Second IE: O > F > N > C

(XII) Electronegativity: B > Al > Ga > In > Tl

(XIII) Electron affinity: Cl > Br > F > I

Sol. Nine orders are correct.

These are: I, III, IV, V, VI, VII, IX, X, and XI

Four orders are incorrect:

These are: II, VIII, XII and XIII

Explanation:

(I) Ionic radius $\propto$ –ve charge $\propto \frac{1}{\text{+ve charge}}$

(II) Correct order: $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$

Small size $F^{\ominus}$ ion, have charge density, much more hydrated, thus have less electrical conductivity in aq. Solution.

$\therefore$ Electrical conductivity in aqueous solution:

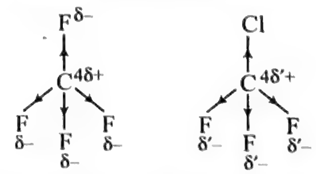
$$\propto \frac{1}{\text{charge density}} \propto \frac{1}{\text{more hydrated ion}}$$

(III) Hydration energy $\propto$ charge density

(IV) Lewis acid character = vacant d-orbital > vacant $3p$ orbital > vacant $2p$ orbitals.

(V) Lattice energy $\propto$ Comparable sizes of the ions $\propto$ ionic character.

(VI) EN of central atom $\propto$ EN of atoms attached to central atom



Since $\delta > \delta^1$, hence C-atom in CF_4 is more EN than in CCl_4.

(VII) Lewis basic character $\propto$ weaker acid $\propto$ stronger conjugate base.

Acidic character order: HI > HBr > HCl > HF

Conjugated base order: $I^{\ominus} < Br^{\ominus} < Cl^{\ominus} < F^{\ominus}$

Thus $F^{\ominus}$ is stronger conjugate base, thus Lewis basic character is higher.

(VIII) Correct order: Pt > Pd > Ni

IE_1 of $5d$ > IE_1 of $4d$ > IE_1 $3d$ series.

This is due to imperfect (weak) shielding of one electron by another in same set of orbitals. However, the shielding of one 4*f* electron by another is less than that of one *d*-electron by another and as the nuclear charge increases along the series, there is fairly increase in IE_1 of 5*d* elements. The IE of 3*d* and 4*d* are irregular.

(IX) Due to inert pair effect, stability of higher O.S. decreases down the group.

(X)

	14	15	16	17
4th Period	Ge	As	Se	Br

Metallic character decreases →

Non metallic character increases →

(XI) (i) $O = 2s^2\,2p^4$, $O^{\oplus} = 2s^2\,2p^3$ (stable configuration)

$O^{2+} = 2s^2\,2p^2$ (It requires very high energy to remove an e^- from stable configuration)

(ii) $F = 2s^2\,2p^5$, $F^{\oplus} = 2s^2\,2p^4$, $F^{+2} = 2s^2\,2p^3$ (stable configuration)

It requires less energy than O-atom to remove second e^-, since it acquires stable configuration.

(iii) $N = 2s^2\,2p^3$, $N^{\oplus} = 2s^2\,2p^3$ $N^{+2} = 2s^2\,2p^1$

IE_1 of N is higher, since e^- has to be removed from stable configuration, but IE_2 is less than F and O.

(IV) $C = 2s^2\,2p^2$, $C^{\oplus} = 2s^2\,2p^1$ $C^{+2} = 2s^2$

IE_2 of C is less than F, O and N, since removal of second e^-, acquire a stable configuration.

(XII) Correct order:

	B	>	Tl	>	In	>	Ga	>	Al
EN =	2.0		1.8		1.7		1.6		1.5

EN first decreases from B to Al due to increase in size. Due to poor shielding effect of *d* and *f*-orbitals, EN increases from Al to Tl.

(XIII) Correct order:

Cl > F > Br > I

Due to very small size of F atom, there is strong $e^- - e^-$ repulsion in relatively small 2*p* orbitals of F, thus incoming e^- is not added easily as it is added in large 3*p*-orbitals of Cl.

EXAMPLE 1.35

Give the names of seven *f*-orbitals and how they are represented.

Sol. A complete set of seven *f*-orbitals is shown in the table and the figure given here.

As with *d*-orbitals, there is no unique way of representing them, nor is there even a way which is optimum for all problems.

The figure presents two sets, a 'General set' and a 'cubic set'. The latter is advantageous in considering the properties of the orbitals in cubic (i.e. octahedral and tetrahedral fields).

Table: Names and shapes of *f*-orbitals

The general set	The cubic set
1. xz^2 **2.** $x(x^2 - 3y^2)$ **3.** $y(3y^2 - x^2)$ Same as $x(x^2 - 3y^2)$ except lies along the *y*-axis. **4.** $z(x^2 - y^2)$ or xyz Same as the corresponding orbitals in the cubic set	**5.** z^3 or x^3 or y^3. i. x^3 same as z^3 except lies along the *x*-axis. ii. y^3 same as z^3 except lies along the *y*-axis **6.** xyz **7.** $z(x^2 - y^2)$ or $y(z^2 - x^2)$ $z(x^2 - y^2)$ Same as xyz but rotated 45° about the *x*, *y*, *z* axes

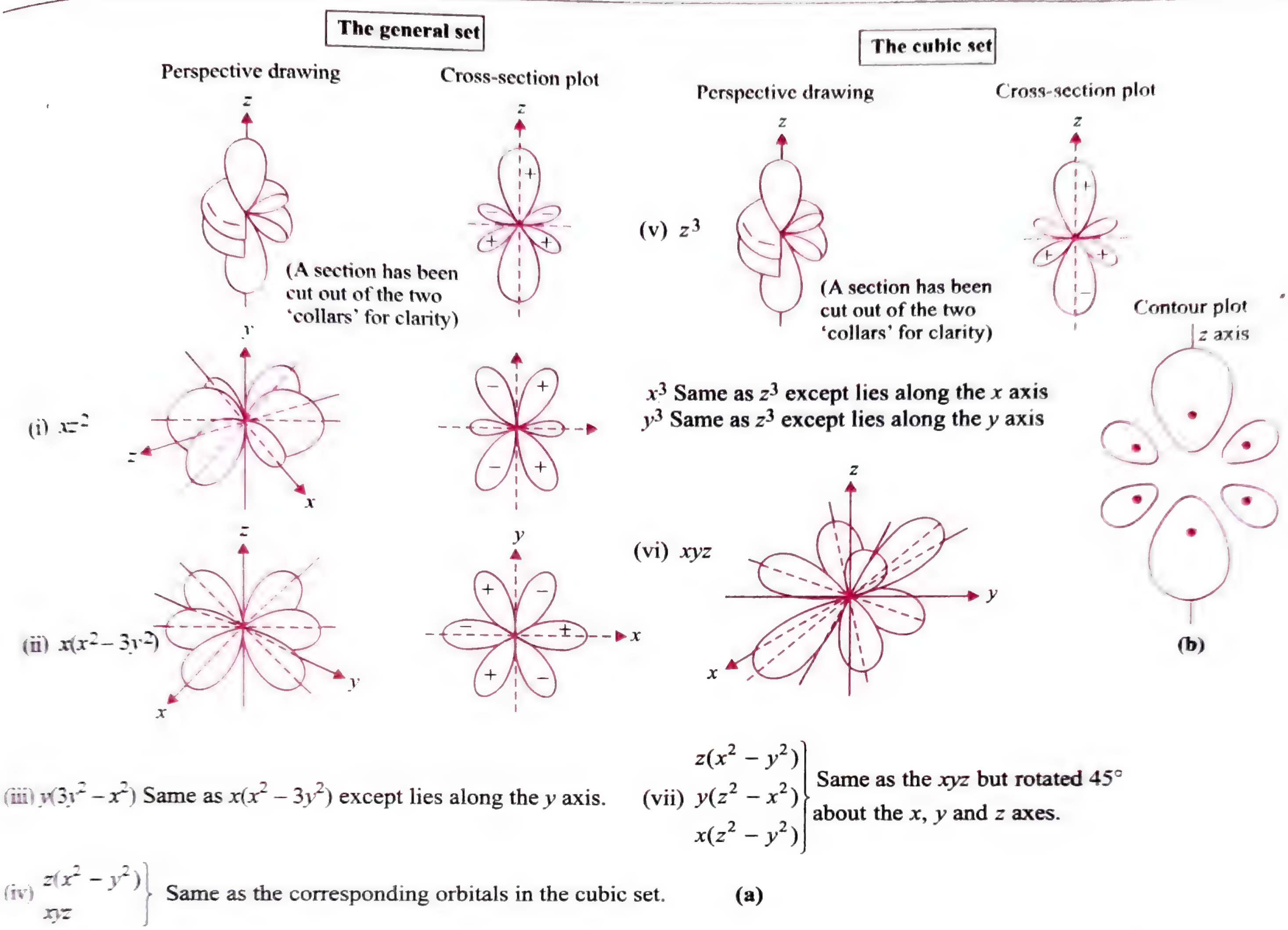


Fig. The *f*-orbitals: (a) Plots of the angular part of the wave functions of the *f* orbital; (b) contours of a 4*f* orbital. Dots indicate maxima in electron density. The lines are drawn for densities which are 10% of maximum.

Exercises

Single Correct Answer Type

General Electronic Configuration and Periodicity

1. According to modern periodic law, the chemical properties of elements are the periodic functions of their
   (1) Atomic mass (2) Atomic number
   (3) Density (4) Mass number
2. Newlands' law of octave applies to which of the following set of elements?
   (1) Be, Mg, Ca (2) As, K, Ca
   (3) B, N, C (4) None of these
3. The element whose electronic configuration is $1s^2$, $2s^2\ 2p^6$, $3s^2$ is a/an
   (1) Metal (2) Metalloid
   (3) Inert gas (4) Non–metal
4. The number of periods and groups in the long form of periodic table are
   (1) 7 and 9 (2) 8 and 18
   (3) 7 and 18 (4) 6 and 10
5. The elements of group 1, 2, 13, 14, 15, 16, 17, 18 are collectively called
   (1) Noble elements (2) Typical elements
   (3) Transition elements (4) Representative elements
6. The statement that is false regarding the long form of the periodic table is
   (1) It reflects the sequence of filling the electrons in the order of sub-energy levels *s*, *p*, *d* and *f*.
   (2) It helps to predict the stable valency states of the elements.
   (3) It reflects trends in physical and chemical properties of the elements.
   (4) It helps to predict the relative ionic character of the bond between any two elements.
7. In the periodic table, going down in group 17
   (1) Reactivity will increase
   (2) Electronegativity will increase
   (3) Ionic radius will increase
   (4) Ionisation potential will increase
8. In the long form of periodic table all the non-metals are placed under
   (1) *s*-block (2) *p*-block
   (3) *d*-block (4) *f*-block
9. Alkali metals in each period have
   (1) Smallest size (2) Highest EN
   (3) Lowest IE (4) Highest IE
10. Which one pair of atoms or ions will have same configuration?
    (1) $F^{\oplus}$ and Ne (2) $Li^{\oplus}$ and $He^{\ominus}$
    (3) Na and K (4) $Cl^{\ominus}$ and Ar
11. In the modern periodic table, the period indicates the v... of
    (1) Atomic number
    (2) Atomic mass
    (3) Principal quantum number
    (4) Azimuthal quantum number
12. Which of the following does not reflect periodicity elements?
    (1) Bonding behaviour (2) EN
    (3) IE (4) Neutron/proton ratio
13. The 3rd period of the periodic table contains
    (1) 8 elements (2) 32 elements
    (3) 3 elements (4) 18 elements
14. Which of the following set contains pair of elements that not belong to same group but show chemical resemblance
    (1) Hf, Zr (2) K, Rb
    (3) Be, Al (4) B, Al
15. Which of the following belongs to the category of transition metal?
    (1) K (2) Ra
    (3) Fe (4) All of the above
16. Without looking at the periodic table, select the elements belonging to same group from the following list.
    (1) $Z = 12, 38, 4, 88$ (2) $Z = 9, 16, 3, 35$
    (3) $Z = 5, 11, 27, 19$ (4) $Z = 24, 47, 42, 55$
17. The elements of same group of the periodic table have
    (1) Same number of protons (2) Same valence shell
    (3) Same valence electrons (4) Same electron affinity
18. The elements which are characterised by the outer shell configuration ns^1 to $ns^2\ np^6$ are collectively called
    (1) Transition elements (2) Representative elements
    (3) Lanthanides (4) Inner transition elements
19. The outer most electronic configuration of transition elements is
    (1) ns^2nd^{1-10} (2) $(n-1)d^{1-10}ns^{1-2}$
    (3) $(n-1)d^2ns^{0-2}$ (4) $(n-1)d^{1-10}ns^2$
20. An element with atomic number 20 is placed in which period of the periodic table?
    (1) 4 (2) 3
    (3) 2 (4) 1
21. The statement that is not correct for periodic classification of elements is
    (1) The properties of elements are the periodic functions of their atomic numbers.
    (2) Non-metallic elements are less in number than metallic elements.
    (3) The first ionisation energies of elements along a period do not vary in a regular manner with an increase in atomic number.

(4) For transition elements the ionisation energies increase gradually with increase in atomic number.

22. In the modern periodic table, elements are arranged in
(1) Increasing mass
(2) Increasing volume
(3) Increasing atomic number
(4) Alphabetically

23. The heaviest element among the following is
(1) U (2) Ra
(3) Pb (4) Hg

24. The screening effect of d-electron is
(1) Equal to p-electron
(2) Much more than p-electron
(3) Same as f-electrons
(4) Less than p-electrons

25. Which of the following represents the electronic configuration of the most electropositive element?
(1) $[He]2s^1$ (2) $[Xe]6s^1$
(3) $[He]2s^2$ (4) $[Xe]6s^2$

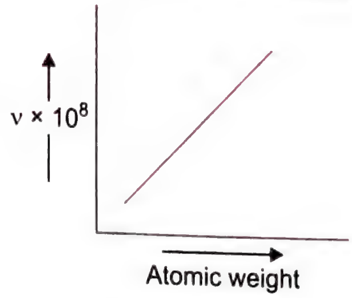
26. Which of the following statement is wrong?
(1) Among the following elements:
K, Mn, Ca, Cs, Fe, Cu, Pb, Os, Y
The number of transition element is 4.
(2) All the lanthanides and actionides belong to III B or the 3rd group in the periodic table.
(3) The inner transition elements belong to the f-block of the periodic table and are shown separately at the bottom of the periodic table.
(4) The d-block elements have variable valency.

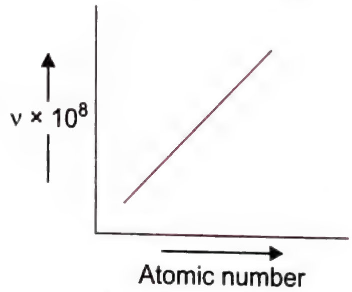
27. Which of the following statement is wrong:
(1) In the lanthanide series the electrons occupy 4f-orbitals in preference to 5d the and 6p-orbitals.
(2) Zero group was not present in the periodic table when Mendeleev presented it.
(3) Law of octave was presented by Newland.
(4) Cuprous compounds are coloured while cupric compounds are colourless.

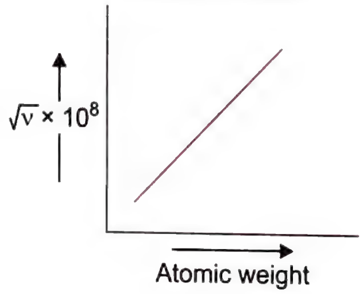
28. Which of the following triads have approximately equal size?
(1) $Na^{\oplus}$, Mg^{2+}, Al^{3+} (isoelectronic)
(2) $F^{\ominus}$, Ne, O^{2-} (isoelectronic)
(3) Fe, Co, Ni
(4) Mn^{1+}, Fe^{2+}, Cr (isoelectronic)

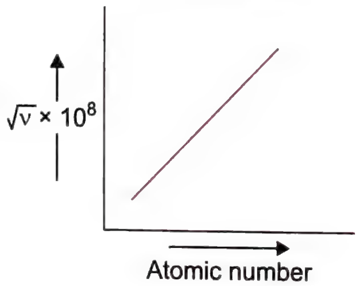
29. Which is the correct order of size?
($O^{\ominus}$, O^{2-}, $F^{\ominus}$ and F ?)
(1) $O^{2-} > O^{\ominus} > F^{\ominus} > F$ (2) $O^{\ominus} > O^{2-} > F^{\ominus} > F$
(3) $O^{2-} > F^{\ominus} > F > O^{\ominus}$ (4) $O^{2-} > F^{\ominus} > O^{\ominus} > F$

30. Select the correct statement:
Which of the following graph represents Moseley's experiment.
(ν = frequency of X-rays)

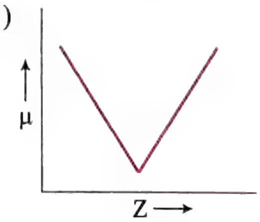
(1)


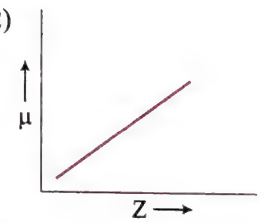
(2)


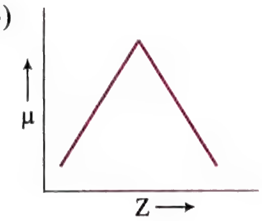
(3)


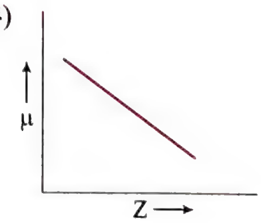
(4)


31. Which of the following graph is correct for elements with outer electronic configuration: $(n-1)d^x\, ns^{1 \text{ or } 2}$.
Z = atomic number
m = magnetic moment

(1)


(2)


(3)


(4)


32. Select correct statement
(1) Sets of atomic numbers 8, 16, 34, 52 corresponds to elements of group 16.
(2) Amongst Fe^{+3}, Cr and $Cu^{\oplus}$, Cr has maximum number of electrons in 'dxy' orbital.

(3) EN and IE both increases down the group in the periodic table.

(4) Element 'X' with electronic configuration, [Xe] $4f^{14} 5d^1 6s^2$ belongs to 6th period and 2nd group.

33. Select incorrect statement

(1) Among $Li^{\ominus}$ and $Be^{\ominus}$, $Be^{\ominus}$ is most unlikely to exist.

(2) The period number and group number of any representative element(s) are same, then elements in their ground state has the possible value of $n = 2, l = 0$

(3) Amongst Mn, Be, Rb and Tl, Rb is most electropositive (metallic) in nature

(4) If there are three possible value $\left(-\frac{1}{2}, 0, +\frac{1}{2}\right)$ for the spin magnetic quantum number m_s, then there will be 15 elements in the second period of the periodic table.

34. Ionisation potential of Li and K are 5.4 and 4.3 eV respectively. Ionisation potential of Na will be:

(1) 9.7 eV (2) 4.9 eV
(3) 1.1 eV (4) Cannot be calculated

Atomic and Ionic Radii

35. Which of the following has the largest ionic radius?

(1) Be^{2+} (2) Mg^{2+}
(3) Ca^{2+} (4) Sr^{2+}

36. The size of species I, $I^{\oplus}$ and $I^{\ominus}$ decreases in the order

(1) $I^{\oplus} > I^{\ominus} > I$ (2) $I^{\ominus} > I > I^{\oplus}$
(3) $I^{\ominus} > I^{\oplus} > I$ (4) $I > I^{\oplus} > I^{\ominus}$

37. Which of the following is smallest in size ?

(1) $Na^{\oplus}$ (2) N^{3-}
(3) O^{2-} (4) $F^{\ominus}$

38. Which of the following represent increasing order of size of 4th period element?

(1) K, Kr, Ca, Br (2) Kr, Br, Ca, K
(3) K, Ca, Br, Kr. (4) Br, Kr, Ca, K

39. Which of the following van der Waals radii is the largest?

(1) Ne (2) Cl
(3) O (4) F

40. The correct order of the size of C, N, P and S is

(1) $N < C < P < S$ (2) $C < N < P < S$
(3) $N < C < S < P$ (4) $C < N < S < P$

41. The correct order of the size of Be, C, F and Ne is

(1) $Be > C > F > Ne$ (2) $Be < C < F < Ne$
(3) $F < Ne < Be < C$ (4) $Be > C > F < Ne$

42. The correct order of increasing radii are

(1) Be^{2+}, Mg^{2+}, $Na^{\oplus}$ (2) $K^{\oplus}$, Ca^{2+}, S^{2-}
(3) O^{2-}, $F^{\ominus}$, N^{3-} (4) S^{2-}, O^{2-}, As^{3-}

43. The correct arrangement of decreasing order of atomic radius among Na, K, Mg and Rb is

(1) $Rb > Na > K > Mg$ (2) $K > Rb > Na > Mg$
(3) $Rb > K > Na > Mg$ (4) $Mg > Rb > K > Na$

44. Which of the following pairs of elements have almost similar atomic radii?

(1) Zr, Hf (2) Cu, Ag
(3) Sc, Ti (4) Pd, Pt

45. The radius of isoelectronic species

(1) Increases with increase in nuclear charge
(2) Decreases with increase in nuclear charge
(3) Same for all
(4) First increases and then decreases

46. Atomic radii of fluorine and neon (Å) respectively are given as

(1) 0.72,1.60 (2) 1.60, 1.60
(3) 0,72, 0.72 (4) 1.60, 0.72

47. Anything that influences the valence electrons will affect the chemistry of the element. Which one of the following factors does not affect the valence shell?

(1) Valence principal quantum number (n)
(2) Nuclear charge (Z)
(3) Nuclear mass
(4) Number of core electrons

48. The size of isoelectronic species $F^{\ominus}$, Ne and $Na^{\oplus}$ is affected by

(1) Nuclear charge (Z)
(2) Valence principal quantum number (n)
(3) Electron–electron interaction in the outer orbitals
(4) None of the factors because their size is the same

49. Ionic radii of

(1) $^{35}Cl^{\ominus} > {}^{37}Cl^{\ominus}$ (2) $Mn^{7+} > Ti^{4+}$
(3) $K^{\oplus} > Cl^{\ominus}$ (4) $P^{3+} > P^{5+}$

50. Which of the following triads have approximatley equal size?

(1) $Na^{\oplus}$, Mg^{2+}, Al^{3+} (isoelectronic)
(2) $Mn^{\oplus}$, Fe^{2+}, Cr (isoelectronic)
(3) $F^{\ominus}$, Ne, O^{2-} (isoelectronic)
(4) Fe, Co, Ni

51. Which of the following species have correct order of size?

(1) $O^{2-} > O^{\ominus} > F^{\ominus} > F$ (2) $O^{\ominus} > O^{2-} > F^{\ominus} > F$
(3) $O^{2-} > F^{\ominus} > O^{\ominus} > F$ (4) $O^{2-} > F^{\ominus} > F > O^{\ominus}$

Effective Nuclear Charge (Z_{eff})

52. Which of the following statement is most correct? Effective nuclear charge of atom depends on

(1) The charge on the ion
(2) The atomic number of an atom
(3) The screening effect
(4) Both (1) and (3)

53. The shielding effect of d-electrons is

(1) More than s-electrons (2) More than p-electrons
(3) Less than s-electrons (4) Same as f-electrons

54. The chemistry of lithium is very similar to that of magnesium even though they are placed in different groups. Its reason is

(1) Both are found together in nature
(2) Both have nearly the same size

(3) Both have similar electronic configuration

(4) The ratio of their charge and size (i.e. charge density) is nearly the same

55. In a given energy level, the order of penetration effect of different orbitals is

(1) $f < d < p < s$ (2) $s = p = d = f$
(3) $s < p < d < f$ (4) $p > s > d > f$

56. Which one of the following group of atoms or ions is not isoelectronic?

(1) He, $H^{\ominus}$, $Li^{\oplus}$ (2) $Na^{\oplus}$, Mg^{2+}, Al^{3+}
(3) $F^{\ominus}$, O^{2-}, N^{3-} (4) $K^{\oplus}$, Ca^{2+}, Ne

57. The correct order of relative stability of half filled and completely filled sub-shell is

(1) $p^3 > d^5 < d^{10} < p^6$ (2) $d^5 > p^3 < d^{10} < p^6$
(3) $d^5 < p^3 < d^{10} < p^6$ (4) $p^3 > d^{10} < d^5 < p^6$

Ionisation Energy (IE)

58. From the ground state electronic configurations of the elements given below, pick up the one with the highest value of second ionisation energies

(1) $1s^2, 2s^2\,2p^6, 3s^2$ (2) $1s^2, 2s^2\,2p^6, 3s^1$
(3) $1s^2, 2s^2\,2p^6$ (4) $1s^2, 2s^2\,2p^5$

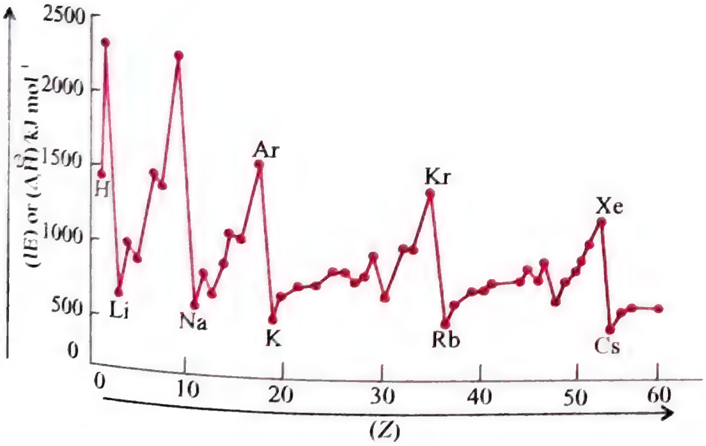
59. Which of the following process refers to IE_2?

(1) $X_{(g)} \rightarrow X^{2+}_{(g)}$ (2) $X^{\oplus}_{(g)} \rightarrow X^{2+}_{(g)}$
(3) $X^{\oplus}_{(aq)} \rightarrow X^{2+}_{(g)}$ (4) $X_{(g)} \rightarrow X^{\oplus}_{(g)}$

60. Which of the following statement concerning ionisation energy is not correct?

(1) The IE_2 is always more than the first.
(2) Within a group, there is a gradual increase in ionisation energy because nuclear charge increases.
(3) Ionisation energies of Be is more than B.
(4) Ionisation energies of noble gases are high.

61. The graph of IE_1 or $\Delta_i H_1^{\ominus}$ versus atomic number (Z) is given below:



Which of the following statement is correct?

(1) Alkali metals are at the maxima and noble gases at the minima.
(2) Noble gases are at the maxima and alkali metals at the minima.
(3) Transition elements are at the maxima.
(4) Minima and maxima do not show any regular behaviour.

62. Which of the following isoelectronic ions have the lowest ionisation enthalpy?

(1) $K^{\oplus}$ (2) Ca^{2+}
(3) $Cl^{\ominus}$ (4) S^{2-}

63. For any given element, the second ionisation potential will be —— the first ionisation potential

(1) less than (2) higher than
(3) same (4) depends on the element

64. Which of the following process requires the largest amount of energy?

(1) $Al_{(g)} \longrightarrow Al^{\oplus} + e^-$
(2) $Al^{2+}_{(g)} \longrightarrow Al^{3+} + e^-$
(3) $Al^{\oplus}_{(g)} \longrightarrow Al^{2+} + e^-$
(4) All require same amount of energy

65. Which of the following is an energy consuming process?

(1) $O_{(g)} + e^- \longrightarrow O^{\ominus}_{(g)}$ (2) $Na^{\oplus}_{(g)} + e^- \longrightarrow Na_{(g)}$
(3) $O^{\ominus}_{(g)} + e^- \longrightarrow O^{2-}_{(g)}$ (4) $O^{2-}_{(g)} \longrightarrow O^{\ominus} + e^-$

66. Arrange S, P and As in order of increasing ionisation energy.

(1) S < P < As (2) P < S < As
(3) As < S < P (4) As < P < S

67. The five successive ionisation energies of an element are 800, 2427, 3658, 25024 and 32824 kJ mol^{-1} respectively. The number of valence electron is

(1) 3 (2) 5
(3) 1 (4) 2

68. Which of the following transitions involve maximum amount of energy?

(1) $M^{\ominus}_{(g)} \longrightarrow M_{(g)}$ (2) $M^{\ominus}_{(g)} \longrightarrow M^{\oplus}_{(g)}$
(3) $M^{\oplus}_{(g)} \longrightarrow M^{2+}_{(g)}$ (4) $M^{2+}_{(g)} \longrightarrow M^{3+}_{(g)}$

69. Which of the elements show least values of ionisation within their periods?

(1) Alkaline earth metals (2) Alkali metals
(3) Noble gases (4) Chalcogens

70. Which one of the following has the largest ionisation energy.

(1) $_{11}Na$ (2) $_{19}K$
(3) $_{12}Mg$ (4) $_{37}Rb$

71. Which one of the following elements has the highest ionisation energy?

(1) [Ne] $3s^2 3p^1$ (2) [Ne] $3s^2 3p^3$
(3) [Ne] $3s^2 3p^2$ (4) [Ar] $3d^{10} 4s^2 4p^2$

72. The correct order of the second ionisation potential of carbon, nitrogen, oxygen and fluorine is

(1) C > N > O > F (2) O > N > F > C
(3) O > F > N > C (4) F > O > N > C

73. Which has the largest first ionisation energy?

(1) Na (2) K
(3) Rb (4) Li

74. Which of the following element has the highest ionisation energy?
(1) Carbon (2) Boron
(3) Oxygen (4) Nitrogen

75. The ionisation potential of nitrogen is more than that of oxygen molecules because of
(1) Greater attraction of electrons by the nucleus
(2) Extra stability of the half-filled p-orbitals
(3) Smaller size of nitrogen
(4) More penetrating effect

76. The set representing the correct order of the first ionisation potential is
(1) K > Na > Li (2) Be > Mg > Ca
(3) B > C > N (4) Ge > Si > C

77. The first ionisation potential of which of the element is highest
(1) Na (2) Mg
(3) Al (4) Si

78. Highest ionisation potential in a period is shown by
(1) Alkali metals (2) Transition elements
(3) Halogens (4) Alkaline earth metals

79. The first ionisation energy is maximum for
(1) Na (2) Mg
(3) K (4) Kr

80. What is the order of ionisation energies of the coinage metal?
(1) Cu > Ag < Au (2) Cu > Ag > Au
(3) Cu < Ag < Au (4) Au > Ag < Cu

81. The second ionisation potentials in electron volts of oxygen and fluorine atoms are respectively given by
(1) 35.1, 38.3 (2) 38.3, 38.3
(3) 38.3, 35.1 (4) 35.1, 35.1

82. The value of IE_1, IE_2, IE_3 and IE_4 of an atom are respectively 7.5 eV, 25.6 eV, 48.6 eV and 170.6 eV. The electronic configuration of the atom will be
(1) $1s^2\,2s^2\,2p^6\,3s^1$ (2) $1s^2\,2s^2\,2p^6\,3s^2\,3p^1$
(3) $1s^2\,2s^2\,2p^6\,3s^2\,3p^3$ (4) $1s^2\,2s^2\,2p^6\,3s^2$

83. IE_1, IE_2 and IE_3 values are 100, 150 and 1500 eV respectively. The element can be
(1) Na (2) B
(3) Be (4) F

84. $N_0/2$ atoms of $X_{(g)}$ are converted into $X^{\oplus}_{(g)}$ by energy E_1, $N_0/2$ atoms of $X_{(g)}$ are converted into $X^{\ominus}_{(g)}$ by energy E_2. Hence ionisation potential and electron affinity of $X_{(g)}$ per atom are
(1) $\dfrac{2E_1}{N_0}, \dfrac{2(E_2 - E_1)}{N_0}$ (2) $\dfrac{2E_1}{N_0}, \dfrac{2E_2}{N_0}$
(3) $\dfrac{(E_1 - E_2)}{N_0}, \dfrac{2E_2}{N_0}$ (4) None is correct

85. Which of the following ionisation energy values for calcium show a sudden increase?
(1) Third (2) Second
(3) First (4) Fourth

86. Which one of the following statements is incorrect in relation to ionisation enthalpy?
(1) Ionisation enthalpy increases for each successive electron.
(2) The greatest increase in ionisation enthalpy is experienced on removal of electron from core noble gas configuration.
(3) End of valence electrons is marked by a big jump in ionisation enthalpy.
(4) Removal of electron from orbitals bearing lower n value is easier than from orbital having higher n value.

87. IE_2 for an element is invariably higher then IE_1 because
(1) It is difficult to remove electron from cation
(2) The size of the cation is smaller than its atoms
(3) Z_{eff} is more for cation
(4) All the above

88. Which of the following metal requires radiation of the lowest wavelength to cause emission of electrons?
(1) Na (2) K
(3) Mg (4) Ca

89. Which has the maximum IE?
(1) $O^{\oplus}$ (2) N
(3) O (4) Na

90. Compound XY is predominantly ionic as $X^{\oplus}Y^{\ominus}$ if
(1) $(IE)_X < (IE)_Y$ (2) $(EA)_X < (EA)_Y$
(3) $(EN)_X < (EN)_Y$ (4) $(IE)_Y < (IE)_X$.

91. The correct order of IE_2 of C, N, O and F is
(1) O > F > N > C (2) F > O > N > C
(3) C > N > O > F (4) O > N > F > C

92. The least stable ion among the following is
(1) $Li^{\oplus}$ (2) $B^{\ominus}$
(3) $C^{\ominus}$ (4) $Be^{\ominus}$

93. Which has the most stable +2 oxidation state?
(1) Sn (2) Fe
(3) Pb (4) Ag

94. Among the following elements (whose electronic configuration are given below) the one having the highest IE is
(1) [Ne] $3s^2\,3p^3$ (2) [Ne] $3s^2\,3p^1$
(3) [Ne]] $3s^2\,3p^2$ (4) [Ar] $3d^{10}\,4s^2\,4p^3$

95. Select the incorrect statement.
(1) IE_1 of C^{2+} > IE_1 of N^{2+}
(2) IE_2 of Se > IE_2 of As
(3) IE_3 of F > IE_3 of O
(4) Halogens have highest IE in respective period

96. If IE and EA of an element are 280 and 90 Kcal mol^{-1} respectively then EN of the element on Pauling scale is:
(1) 2.96 (2) 2.6
(3) 0 (4) 4.0

97. Aqueous solution of two compounds A–O–H and B–O–H are taken separately. If the EN of A = 3.0, B = 1.5, O = 3.5 and H = 2.1, then the nature of two solutions will be respectively

(1) Both acidic (2) Both basic
(3) Acidic, basic (4) Basic, acidic

98. Consider the following ionisation reactions:

Reactions	IE
(i) $X(g) \longrightarrow X^{\oplus}(g) + e^-$	X_1
(ii) $Y(g) \longrightarrow Y^{\oplus}(g) + e^-$	Y_1
(iii) $Y^{\oplus}(g) \longrightarrow Y^{+2}(g) + e^-$	Y_2
(iv) $Z(g) \longrightarrow Z^{\oplus}(g) + e^-$	Z_1
(v) $Z^{\oplus}(g) \longrightarrow Z^{+2}(g) + e^-$	Z_2
(vi) $Z^{+2}(g) \longrightarrow Z^{+3}(g) + e$	Z_3

If $Y^{\oplus}$, Y^{+2} and Z^{+3} ion have zero electron.

Select the incorrect order of corresponding IE.

(1) $Y_1 > X_1 > Z_1$ (2) $Y_2 > Z_3 > Z_1$
(3) $Z_3 > Y_2 > X_1$ (4) $Z_3 > Z_2 > Y_2$

Isoelectronic Species

99. Which of the following are isoelectronic?

$NO_3^{\ominus}$, CO_3^{2-}, $ClO_3^{\ominus}$, SO_2

(1) $NO_3^{\ominus}$, CO_3^{2-}, $ClO_3^{\ominus}$ (2) $NO_3^{\ominus}$, CO_3^{2-}, SO_2
(3) CO_3^{2-}, $ClO_3^{\ominus}$, SO_2 (4) None of these

100. Consider the isoelectronic series, $K^{\oplus}$, S^{2-}, $Cl^{\ominus}$, Ca^{2+}, the radii of the ions decrease as

(1) $Ca^{2+} > K^{\oplus} > Cl^{\ominus} > S^{2-}$ (2) $Cl^{\ominus} > S^{2-} > K^{\oplus} > Ca^{2+}$
(3) $S^{2-} > Cl^{\ominus} > K^{\oplus} > Ca^{2+}$ (4) $K^{\oplus} > Ca^{2+} > S^{2-} > Cl^{\ominus}$

101. Which of the following are isoelectronic species?

$\overset{\oplus}{C}H_3$ (I), $\overset{\ominus}{N}H_2$ (II), $\overset{\oplus}{N}H_4$ (III) and NH_3 (IV)

(1) II, III and IV (2) I, II and III
(3) I, II and IV (4) II and I

102. Two *p*-block elements *x* (outer configuration $ns^2\ np^3$) and *z* (outer configuration $ns^2\ np^4$) occupy neighbouring positions in a period. Using this information which of the following is correct with respect to their ionisation potential I_x and I_z.

(1) $I_x > I_z$
(2) $I_z > I_x$
(3) $I_z = I_x$
(4) Relation between I_x and I_x is uncertain

Metallic–Non-metallic Character

103. Considering the elements B, Al, Mg and K, the correct order of their metallic character is

(1) B > Al > Mg > K (2) Al > Mg > B > K
(3) Mg > Al > K > B (4) K > Mg > Al > B

104. IE_1 and IE_2 of Mg are 178 and 348 kcal mol^{-1}. The energy required for the reaction $Mg \longrightarrow Mg^{2+} + 2e^-$ is

(1) +170 kcal (2) +526 kcal
(3) –170 kcal (4) –526 kcal

105. Considering the elements B, C, N and Si, the correct order of their non-metallic character is?

(1) B > C > Si > N > F (2) Si > C > B > N > F
(3) F > N > C > B > Si (4) F > N > C > Si > B

Electron Affinity (EA) and Electron Gain Enthalpy ($\Delta_{eg}H^{\ominus}$)

106. Which of the following have least electron affinity?

(1) Oxygen (2) Fluorine
(3) Nitrogen (4) Carbon

107. Second and successive electron affinity of an element

(1) is always successive (energy is released)
(2) is always positive (energy is absorbed)
(3) can be positive or negative
(4) is always zero

108. Which one of the following statements is incorrect?

(1) Greater is the nuclear charge, greater is the electron affinity.
(2) Neon has zero electron affinity.
(3) Electron affinity decreases from fluorine to iodine in the group.
(4) Electron affinity decreases in going down a group and increases across period from the left to the right (→).

109. The lower electron affinity of fluorine than that of chlorine is due to

(1) Smaller size
(2) Smaller nuclear charge
(3) Difference in their electronic arrangement
(4) Its highest reactivity

110. The EA order for halogen is

(1) F > Cl > Br > I (2) F < Cl < Br < I
(3) F < Cl > Br > I (4) F > Cl < Br < I

111. The EA for inert gases is likely to be

(1) High (2) Small
(3) Zero (4) Positive

112. Ionisation of energy $F^{\ominus}$ is 320 kJ mol^{-1}. The electron gain enthalpy of fluorine would be

(1) –320 kJ mol^{-1} (2) –160 kJ mol^{-1}
(3) +320 kJ mol^{-1} (4) +160 kJ mol^{-1}

113. Which of the following represents the correct order of electron affinities?

(1) F > Cl > Br > I (2) C < N < O < F
(3) N < C < O < F (4) C < Si < P < N

114. Fluorine has the highest electronegativity among the group on the Pauling scale, but the electron affinity of fluorine is less than that of chlorine because

(1) The atomic number of fluorine is less than that of chlorine
(2) Fluorine being the first member of the family behaves in an unusual manner
(3) Chlorine can accommodate an electron better than fluorine by utilising its vacant 3*d* orbital
(4) Small size, high electron density and an increased electron repulsion make addition of an electron to fluorine less favourable than that in the case of chlorine

115. EA is positive when

(1) $O^{\ominus}$ is formed from O (2) $O^{\oplus}$ is formed from O
(3) O^{2-} is formed from O
(4) EA is always a negative value

Electronegativity (EN)

116. Which is true about the electronegativity order of the following elements?
   (1) P > Si (2) C > N
   (3) Br > Cl (4) Sr > Ca

117. The electronegativity of the following elements increases in the order
   (1) C, N, Si, P (2) N, Si, C, P
   (3) Si, P, C, N (4) P, Si, N, C

118. An atom with high EA generally has
   (1) Tendency to form +ve ions
   (2) High ionisation energy
   (3) Large atomic size
   (4) Low electron affinity

119. The electronegativity of the following elements increases in the order
   (1) S < P < N < O (2) P < S < N < O
   (3) N < O < P < S (4) N < P < S < O

120. Downwards in a group, the electropositive character of elements
   (1) Increases (2) Decreases
   (3) Remains same (4) None

121. What is the correct order of electronegativity?
   (1) $M^{1-} < M^{2-} < M^{3-} < M^{4-}$ (2) $M^{1-} > M^{2-} > M^{3-} > M^{4-}$
   (3) $M^{1-} < M^{2-} > M^{3-} < M^{4-}$ (4) $M^{4-} < M^{2-} < M^{3-} < M^{1-}$

122. Due to screening effect of electrons in an atom
   (1) IE decreases
   (2) IE increases
   (3) No change in IE
   (4) Attraction of nucleus on the valence electron increases

123. Select the group where EN increases down the group
   (1) F, Cl, Br (2) Li, Na, K
   (3) Ca, Sr, Ba (4) Zn, Cd, Hg

124. Which of the following element has the highest EN?
   (1) As (2) Sb
   (3) P (4) S

125. The electronegativity values of C, N, O and F
   (1) Increases from carbon to fluorine
   (2) Decreases from carbon to fluorine
   (3) Increases up to oxygen and is minimum at fluorine
   (4) Is minimum at nitrogen and then increases continuously

126. EN value for four elements A, B, C and D are respectively 2.7, 2.1, 0.8 and 3.4. select incorrect statement based on given above data.
   (1) Compound AB conducts electricity only in fused state
   (2) Compound BD conducts electricity only in solution state.
   (3) Compound CD conducts electricity in fused as well in solution state.
   (4) AD does not conduct electricity in solid and fused state.

Acidic, Basic and Amphoteric Character

127. Among the following oxides, which is least acidic?
   (1) Al_2O_3 (2) B_2O_3
   (3) CO_2 (4) NO_2

128. Which of the following oxides is most basic?
   (1) Na_2O (2) MgO
   (3) Al_2O_3 (4) CuO

129. The order of which of the following oxides is arranged according to decreasing basic nature?
   (1) Na_2O, MgO, Al_2O_3, CuO (2) CuO, Al_2O_3, MgO, Na_2O
   (3) Al_2O_3, CuO, MgO, Na_2O (4) CuO, MgO, Na_2O, Al_2O_3

130. The correct order of acidic strengths of the following is
   (1) $CaO < CuO < H_2O < CO_2$
   (2) $CaO < H_2O < CuO < CO_2$
   (3) $H_2O < CuO < CaO < CO_2$
   (4) $H_2O < CO_2 < CaO < CuO$

131. What is the nature of Al_2O_3 and B_2O_3?
   (1) Acidic, acidic (2) Acidic, amphoteric
   (3) Amphoteric, amphoteric (4) Amphoteric, acidic

132. Which of the following oxides is neutral?
   (1) SiO_2 (2) CO
   (3) ZnO (4) SnO_2

133. Which of the following oxides is amphoteric in nature?
   (1) CaO (2) CO_2
   (3) SnO_2 (4) SiO_2

134. The correct order of acidic strength of the following is
   (1) $SO_2 > P_2O_3 > SiO_2 > Al_2O_3$
   (2) $P_2O_3 > SO_2 > SiO_2 > Al_2O_3$
   (3) $P_2O_3 > Al_2O_3 > SO_2 > SiO_2$
   (1) $Al_2O_3 > SiO_2 > P_2O_3 > SO_2$

135. Which of the oxides behaves both as suboxide and as neutral oxide?
   (1) CO (2) CO_2
   (3) C_3O_2 (4) N_2O

136. Which of the oxides is not a mixed oxide?
   (1) $Co(Al_2O_2)_2$ (2) Mn_3O_4
   (3) Pb_3O_4 (4) C_3O_2

137. Which of the oxides is basic as well as normal oxide?
   (1) N_2O (2) Na_2O
   (3) NO (4) H_2O

138. Which is/are amphoteric oxide?
   (1) ZnO (2) BeO
   (3) SnO (4) All of these

139. (X), (Y), (Z) are elements in third short period. Oxide of (X) is ionic, (Y) is amphoteric and (Z) is a giant molecule. (X), (Y) and (Z) will have atomic number in the order:
   (1) (X) < (Y) < (Z) (2) (Z) < (Y) < (X)
   (3) (X) < (Z) < (Y) (4) (Y) < (X) < (Z)

Bond Angle

140. Decreasing order of bond angle of (NH_3, PH_3, AsH_3) is
   (1) $NH_3 > PH_3 > AsH_3$ (2) $NH_3 > AsH_3 > PH_3$
   (3) $PH_3 > NH_3 > AsH_3$ (4) $AsH_3 > PH_3 > NH_3$

141. Decreasing order of bond angle of ($NO_2^{\oplus}$, NO_2, $NO_2^{\ominus}$) is
(1) $NO_2^{\ominus} > NO_2 > NO_2^{\oplus}$ (2) $NO_2^{\oplus} > NO_2 > NO_2^{\ominus}$
(3) $NO_2^{\ominus} > NO_2^{\oplus} > NO_2$ (4) $NO_2 > NO_2^{\ominus} > NO_2^{\oplus}$

142. Decreasing order of bond angle of (NH_3, $\overset{\oplus}{N}H_4$, PCl_5, SCl_2) is
(1) $NH_3 > SCl_2 > PCl_5 > \overset{\oplus}{N}H_4$
(2) $NH_3 > SCl_2 > \overset{\oplus}{N}H_4 > PCl_5$
(3) $\overset{\oplus}{N}H_4 > NH_3 > SCl_2 > PCl_5$
(4) $\overset{\oplus}{N}H_4 > NH_3 > PCl_5 > SCl_2$

143. Increasing order of bond angle of (Cl_2O, ClO_2, Cl_2O_7, $I_3^{\ominus}$) is
(1) $Cl_2O < ClO_2 < Cl_2O_7 < I_3^{\ominus}$
(2) $Cl_2O < ClO_2 < I_3^{\ominus} < Cl_2O_7$
(3) $I_3^{\ominus} < Cl_2O_7 < ClO_2 < Cl_2O$
(4) $Cl_2O < Cl_2O_7 < ClO_2 < I_3^{\ominus}$

144. Which of the following has the smallest bond length?
(1) O_2 (2) N_2
(3) Cl_2 (4) HCl.

145. Bond angle in PH_3 is
(1) Much less than NH_3 (2) Much less than PF_3
(3) Slightly more than NH_3 (4) Much more than PF_3

146. The correct order of decreasing bond angles in H_2S, NH_3, BF_3 and SiH_4 is
(1) $BF_3 > SiH_4 > H_2S > NH_3$
(2) $BF_3 > SiH_4 > NH_3 > H_2S$
(3) $BF_3 > NH_3 > SiH_4 > H_2S$
(4) $SiH_4 > BF_3 > NH_3 > H_2S$

147. The bond angle around central atom is maximum for
(1) H_2O (2) H_2S
(3) H_2Se (4) H_2 Te

Lattice and Hydration Energy

148. Decreasing order of hydration energy of the following is
(1) $Li^{\oplus} > Na^{\oplus} > K^{\oplus} > Cs^{\oplus}$ (2) $Cs^{\oplus} > K^{\oplus} > Na^{\oplus} > Li^{\oplus}$
(3) $Li^{\oplus} > K^{\oplus} > Na^{\oplus} > Cs^{\oplus}$ (4) $Cs^{\oplus} > Na^{\oplus} > K^{\oplus} > Li^{\oplus}$

149. Extent of hydrolysis of the following is
(1) $PCl_5 > SiCl_4 > MgCl_2 > AlCl_3$
(2) $AlCl_3 > MgCl_2 > SiCl_4 > PCl_5$
(3) $SiCl_4 > PCl_5 > MgCl_2 > AlCl_3$
(4) $PCl_5 > SiCl_4 > AlCl_3 > MgCl_2$

150. Give the decreasing order of thermal stability of the following.
(1) Be CO_3 > Mg CO_3 > Ca CO_3 > Ba CO_3
(2) Ba CO_3 > Ca CO_3 > Mg CO_3 > Be CO_3
(3) Be CO_3 > Ca CO_3 > Ba CO_3 > Mg CO_3
(4) Mg CO_3 > Ca CO_3 > Ba CO_3 > Be CO_3

151. Lattice energy of an ionic compound depends on
(1) Charge density of the ion
(2) Packing of ions only
(3) Size of the ion only
(4) Charge on the ions only

152. Na_2SO_4 is soluble in water while $BaSO_4$ is insoluble. Which of the reason is correct about the above statement.
(1) Lattice energy of $BaSO_4$ exceeds its hydration energy.
(2) Hydration energy of $BaSO_4$ exceeds its lattice energy.
(3) The solubility in H_2O of a compound depends only on its hydration energy.
(4) The solubility in H_2O of a compound depends only on its lattice energy.

153. Calculate the lattice energy from the following data (given 1 eV = 23.0 kcal mol^{-1})
i. $\Delta_f H^{\ominus}$ (KI) = − 78.0 kcal mol^{-1}
ii. IE_1 of K = 4.0 eV
iii. $\Delta_{diss}H^{\ominus}$ (I_2) = 28.0 kcal mol^{-1}
iv. $\Delta_{sub}H^{\ominus}$ (K) = 20.0 kcal mol^{-1}
v. EA of I = − 70.0 kcal mol^{-1}
vi. $\Delta_{sub}H^{\ominus}$ of I_2 = 14.0 kcal mol^{-1}
(1) +14.1 kcal mol^{-1} (2) −14.1 kcal mol^{-1}
(3) −141 kcal mol^{-1} (4) +141 kcal mol^{-1}

154. Calculate the EA of O atom to O^{2-} ion from the following data:
i. $\Delta_f H^{\ominus}$ [MgO (s)] = − 600 kJ mol^{-1}
ii. $\Delta_{lt} H^{\ominus}$ [MgO (s)] = − 3860 kJ mol^{-1}
iii. $IE_1 + IE_2$ of Mg (g) = 2170 kJ mol^{-1}
iv. $\Delta_{diss}H^{\ominus}$ [O_2 (g)] = + 494 kJ mol^{-1}
v. $\Delta_{sub}H^{\ominus}$ of Mg (s) = + 150 kJ mol^{-1}
(1) + 693 kJ mol^{-1} (2) − 693 kJ mol^{-1}
(3) + 69.3 kJ mol^{-1} (4) − 69.3 kJ mol^{-1}

155. Which has maximum polarising power in cation?
(1) O^{2-} (2) Al^{+3}
(3) Li^{+} (4) Mg^{+2}

156. Which of the following ions has the highest heat of hydration?
(1) $Na^{\oplus}$ (2) $Li^{\oplus}$
(3) $Cs^{\oplus}$ (4) $K^{\oplus}$

157. In which solvent KBr has maximum solubility?
(1) C_2H_5OH (2) CH_3COCH_3
(3) $C_2H_5OC_2H_5$ (4) H_2O

158. Lattice energy of $BeCO_3$ (I), $MgCO_3$ (II) and $CaCO_3$ (III) is in order.
(1) I > II > III (2) III > II > I
(3) II > III > I (4) III > I > II

159. 'Solubility of groups 1 and 2 fluorides increases down the group'. Which of the following is correct explanation for the above given statement?

(1) Both the hydration and lattice energies decrease down the group (↓) but decrease in lattice energy is rapid.
(2) Both the energies increase down the group but increase in hydration energy is rapid.
(3) Both the energies decrease down the group but decrease in hydration energy is rapid.
(4) Hydration energy increases and lattice energy decreases down the group.

160. The magnitude of lattice energy of a solid increases if
(1) The ions are large
(2) The ions are small
(3) The ions are of equal sizes
(4) Charges on the ions are small

Miscellaneous

161. Which of the following is correct?
(1) With increase in atomic size, ionisation energy increases
(2) With increase in atomic size, electron affinity increases
(3) With increase in atomic size, metallic character increases
(4) With increase in atomic size, electronegativity increases

162. Which of the following is incorrect?
(1) An element which has high electronegativity always has high electron gain enthalpy.
(2) Electron gain enthalpy is the property of an isolated atom.
(3) Electronegativity is the property of bonded atom.
(4) Both electronegativity and electron gain enthalpy are usually directly related to nuclear charge and inversely related to atomic size.

163. The ionisation of hydrogen atom would give rise to
(1) Hydride ion (2) Hydronium ion
(3) Proton (4) Hydroxyl ion

164. Chloride of an element A gives neutral solution in water. In the periodic table, the element A belongs to
(1) First group (2) Third group
(3) Fifth group (4) First transition series

165. In a period, density first __ then __ and in a group it __ down the group
(1) Decreases, increases, remains constant
(2) Increases, decreases, decreases
(3) Increases, remains constant, increases
(4) Increases, decreases, increases

166. In the transformation of Na(s) $\longrightarrow$ $Na^{\oplus}$ (g), the energies involved are
(1) Ionisation energy
(2) Sublimation energy
(3) Ionisation energy and sublimation energy
(4) Bond dissociation energy

167. Beryllium and aluminium exhibit many properties which are similar. But the two elements differ in
(1) Forming covalent halides
(2) Forming polymeric hydrides
(3) Exhibiting maximum covalency in compounds
(4) Exhibiting amphoteric nature in their oxides

168. Among LiCl, $BeCl_2$, BCl_3 and CCl_4 the covalent bond character follows the order
(1) $LiCl > BeCl_2 > BCl_3 > CCl_4$
(2) $LiCl < BeCl_2 < BCl_3 < CCl_4$
(3) $LiCl > BeCl_2 > CCl_4 > BCl_3$
(4) $BeCl_2 > LiCl > BCl_3 > CCl_4$

169. The correct order of polarisability of ion is
(1) $Cl^{\ominus} > Br^{\ominus} > I^{\ominus} > F^{\ominus}$ (2) $F^{\ominus} > I^{\ominus} > Br^{\ominus} > Cl^{\ominus}$
(3) $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$ (4) $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

170. Diagonal relationship is shown by
(1) All elements with their diagonally opposite elements.
(2) All elements of 3rd and 4th periods
(3) Some of the elements of 2nd and 3rd periods
(4) Elements of *d*-block

171. Inert pair effect is shown by
(1) *s*-block (2) *p*-block
(3) *d*-block (4) *f*-block

172. Which has the maximum covalent character?
(1) $MgCl_2$ (2) NaCl
(3) $SiCl_4$ (4) $AlCl_3$

173. NO_2 and N_2O_4 are two forms of nitrogen dioxide. One exists in gaseous state while other in liquid state. The nature of NO_2 and N_2O_4 forms are
(1) Both are diamagnetic
(2) Both are paramagnetic
(3) NO_2 is diamagnetic while N_2O_4 is paramagnetic
(4) NO_2 is paramagnetic while N_2O_4 is diamagnetic

174. Magnetic moments of V (Z = 23), Cr (Z = 24) and Mn (Z = 25) are x, y and z respectively, hence
(1) $x = y = z$ (2) $x < y < z$
(3) $x < z < y$ (4) $z < y < x$

175. Which of the following molecule is theoretically not possible?
(1) OF_4 (2) O_2F_2
(3) OF_2 (4) SF_4

176. Which pair is different from the others?
(1) Na–K (2) Ca–Mg
(3) Li–Mg (4) B–Al

177. The correct order of decreasing ionic character is
(1) $BaCl_2 > CaCl_2 > MgCl_2 > BeCl_2$
(2) $BaCl_2 > MgCl_2 > CaCl_2 > BeCl_2$
(3) $BeCl_2 > MgCl_2 > CaCl_2 > BaCl_2$
(4) $BaCl_2 > BeCl_2 > CaCl_2 > MgCl_2$

178. The correct order of decreasing polarisability of ion is
(1) $Cl^{\ominus} > Br^{\ominus} > I^{\ominus} > F^{\ominus}$ (2) $F^{\ominus} > I^{\ominus} > Br^{\ominus} > Cl^{\ominus}$
(3) $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$ (4) $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

179. An element 'y' present in its ground state, the value of principal and azimuthal quantum number of last electron of element 'y' is $n = 3$, and $l = 1$ and spin multiplicity for given element is 4.

Select incorrect statement based on above information.

(1) Element 'y' is 3rd period and 15th group element

(2) Element 'y' has magnetic moment = $\sqrt{15}$ BM

(3) In valence shell of element 'y' electron density is symmetrically distributed.

(4) Element 'y' is nitrogen.

180. Select incorrect statement

(1) Element 'x' with electronic configuration $(n-1)d^2ns^2$ $(n = 4)$ belong to 4th period and 4th group.

(2) Element 'y' with electronic configuration $(n-2)f^7$ $(n = 1)d^1ns^2$ $(n = 6)$ belongs to 6th period and 3rd group and is lanthanide element.

(3) Element 'z' with electronic configuration ns^2np^2 $(n = 6)$ belong to 3rd period and 16th group.

(4) All x, y, z elements are metals.

181. The value of four quantum numbers for the last electron of atom of element 'P' are $n = 7, l = 1, m = \pm 1$ or $s = +\frac{1}{2}, -\frac{1}{2}$ and value of spin magnetic moment for element 'P' is zero. The element has two isotopes, $^{A}_{Z}P$ and $^{B}_{Z}P$.

Given: $B - A = B - 2Z = 18$, where A and B are atomic masses and Z is atomic number.

Select incorrect statement based upon above information

(1) Element 'P' belongs to 18th group, with $Z = 118$

(2) Element 'P' is representative element.

(3) The value of A and B respectively are 236 and 254.

(4) The possible value of all four quantum numbers for 90th electron of atom of element 'P' is: $n = 5, l = 3, m = -2, s = -\frac{1}{2}$.

Multiple Correct Answers Type

General Electronic Configuration and Periodicity

1. Which of the following statement(s) is/are correct?

(1) Mendeleev's periodic law was based on atomic numbers of the element.

(2) Zero group was not present in the periodic table when Mendeleev presented it.

(3) The effective nuclear charge (Z_{eff}) is the atomic number minus shielding effect.

(4) There are four transition series in the periodic table each one consists of 10 elements.

2. Which of the following statement(s) is/are correct?

(1) Similar electronic configuration is repeated after intervals of 2, 8, 8, 18 and 32 in the extended form of periodic table.

(2) In a period from right to left (←), reducing nature increases.

(3) Along the period (→) the number of valency electrons increases from 1 to 8.

(4) The first member of lanthanide series is lanthanum.

3. Which of the following statement(s) is/are correct?

(1) All the members of the actinide series are man made.

(2) Zero group elements are paramagnetic.

(3) Third group of the periodic table accommodates maximum number of elements.

(4) All members of zero groups are non-metals.

4. Which of the following statements(s) is/are correct?

(1) In Mendeleev periodic table, all groups are divided into two subgroups.

(2) There is no relationship between electronic configuration of the elements and their position in the extended form of periodic table.

(3) s-block elements have one or two electrons in their outermost shell.

(4) Osmium has the maximum density among metals.

5. Which of the following statement(s) is/are correct?

(1) The last member of the 7th period of the periodic table will have atomic number 118 if discovered.

(2) All the transition elements are metals and paramagnetic.

(3) The maximum number of elements are present in the 5th period of the periodic table.

(4) Every period of the periodic table starts with a member of alkali group.

6. These are three elements X, Y and Z. the atomic number are A_1, A_2 and A_3 respectively.

If $A_1 - A_2 = 2$ and

$$\frac{A_1 + A_2}{2} = A_3 - 2$$

and electronic configuration of element X is [Ar] $3d^6 4s^2$ then correct order of magnetic moment are:

(1) $Y > X > Z^{2+}$

(2) $Y^{\oplus} > X^{2+} > Z^{2-}$

(3) $Y = X^{3+} > Z^{3+}$

(4) $X^{+3} > Y^{2+} > Z$

7. Consider the value of all four quantum number of last electron and spin multiplicity (2s + 1) for the given two elements 'A' and 'B' in their ground state

	n	l	m	s	$\lvert 2s+1 \rvert$
A	2	0	0	$\frac{1}{2}$	1
B	2	1	−1	$+\frac{1}{2}$	4

Then according to given information correct statements are:

(1) Magnetic moment of B is greater than A.

(2) A and B element shows only single oxidation state.

(3) The possible halide of 'A' has two vacant p-orbitals on its central atom.

(4) The bond angle (H–N–H) of possible hydride of element 'B' is less than 109° 28'

8. Consider all four quantum number of last electrons and magnetic moment and valence electrons of elements A, B, C and D is their ground state.

Element	n	l	m	s	Magnetic moment (m) B.M.	Valence electrons
A	3	0	0	$+\frac{1}{2}$	0	2
B	3	1	+1	$-\frac{1}{2}$	$\sqrt{3}$	3
C	3	1	−1	$+\frac{1}{2}$	$\sqrt{15}$	5
D	3	1	0	$-\frac{1}{2}$	$\sqrt{8}$	6

According to given information, select the correct statements.

(1) IE_1 of element A > IE_1 of element B
(2) IE_1 of element C > IE_1 of element D
(3) IE_2 of element D > IE_2 of element C
(4) IE_2 of element B > IE_2 of element A

Atomic and Ionic Radii

9. Which of the following is correct in order of increasing size?
(1) $I^{\oplus} < I < I^{\ominus}$ (2) $Fe < Fe^{2+} < Fe^{3+}$
(3) $Fe^{3+} < Fe^{2+} < Fe$ (4) All of the above

10. Reason for diagonal relationship is
(1) Same size (2) Same electronegativity
(3) Same electron affinity (4) Same polarisability

11. Which of the following pairs of elements have almost similar atomic radii?
(1) Zr, Hf (2) Mo, W
(3) Co, Ni (4) Nb, Ta

12. Which of the following statements is/are correct?
(1) An anion is larger than a cation if they are isoelectronic.
(2) Out of $Na^{\oplus}$ and Al^{3+}, $Na^{\oplus}$ has the largest size.
(3) The ionic radii of trivalent lanthanides [La^{3+}, Ce^{3+}, Pr^{3+}, ...] decreases with increasing atomic number.
(4) Out of P^{3-}, S^{2-}, and $Cl^{\ominus}$, $Cl^{\ominus}$ ion has the largest size.

Effective Nuclear Charge (Z_{eff})

13. Which of the following statements(s) is/are correct?
(1) Z_{eff} of elements increases along the period (→).
(2) Z_{eff} of elements increases down the group (↓).
(3) Isoelectronic species have the same nuclear charge.
(4) Screening constant (σ) increases down the group (↓).

Ionisation Energy (IE)

14. Which of the following statement(s) is/are correct?
(1) Successive IE's are lower.
(2) Less energy is required to remove an electron from a half-filled shell or completely filled shell.
(3) IE_1 of Al < IE_1 of Mg
(4) IE_1 of Be > IE_1 of B

15. The factors that influence the ionisation energies are
(1) Size of the atom
(2) Charge on the nucleus
(3) The inner electrons which effectively screen the nuclear charge
(4) Atomic number of the element

16. Which is the correct increasing order of ionisation energy?
(1) Li < B < Be (2) Be < B < Li
(3) Li <Na < K (4) O < N < F

17. Which is correct about ionisation potential?
(1) IE_1 of N > IE_1 of O (2) IE_2 of N > IE_2 of O
(3) IE_2 of Li > IE_2 of Ne (4) IE_1 of Al > IE_1 of Ca

18. The first eight ionisation energies for a particular neutral atom is as given below. All values are expressed in kJ mol^{-1}. Which oxidation state(s) is/are not possible of the atom?

1st	2nd	3rd	4th	5th	6th	7th	8th
1.31	3.39	5.30	7.47	10.99	13.33	71.33	84.01

(1) −2 (2) −3
(3) −6 (4) 6

19. IE_2 for an element is invariably higher than IE_1 because
(1) The size of cations is smaller than its atom.
(2) It is difficult to remove electron from cations.
(3) Ionisation energy is endothermic.
(4) All of the above.

20. Which sequence is correct regarding the first ionisation potential of coinage metals?
(1) Cu > Ag > Au (2) Cu < Ag < Au
(3) Cu > Ag < Au (4) Ag > Cu < Au

21. Mark the correct statements out of the following:
(1) He has highest IE_1 in the periodic table.
(2) Cl has the highest EA out of all elements in the periodic table.
(3) Hg and Br are liquid at room temperature.
(4) In any period, the atomic radius of the noble gas is lowest.

22. Ionisation energy is influenced by
(1) Size of atom
(2) Charge of nucleus
(3) Electrons present in inner shells
(4) None of the above

23. According to Slater's rule, the correct order of Z_{eff} of valence shell electron is:
(1) $Mn^{5+} > V^{3+} > Ti^{2+}$ (2) $F^{\ominus} > O^{2-} > N^{3-}$
(3) $Fe > Fe^{+2} > Fe^{3+}$ (4) $Al^{+3} > Mg^{2+} > Na^{\oplus}$

24. Consider the following value of IE (eV) for elements A and B.

Element	IE_1	IE_2	IE_3	IE_4
A	10.5	15.5	24.9	79.8
B	8.0	14.8	78.9	105.8

Other two elements C and D have outer electronic configuration ns^2np^4 and ns^2np^5 respectively which of the following compounds are possible

(1) A_2C_3 (2) AD_2

(3) BD_2 (4) B_2C_3

Electron Affinity (EA)

25. Which of the following statement(s) is/are correct?

(1) The element which has higher EA acts as a strong oxidising agent.

(2) The element with higher EA has higher IE.

(3) Along a period halogen has maximum EA.

(4) The decreasing order of EA is F > Cl > Br.

26. Which of the following process do not involve absorption of energy?

(1) $Cl(g) + e^- \longrightarrow Cl^{\ominus}(g)$ (2) $S(g) + e^- \longrightarrow S^{\ominus}(g)$

(3) $O(g) + e^- \longrightarrow O^{\ominus}(g)$ (4) $O^{\ominus} + e^- \longrightarrow O^{2-}(g)$

27. Consider the order:

$Mg^{2+} > Na^{\oplus} > F^{\ominus} > O^{2-}$

Then correct statements are:

(1) Decreasing order of I.E.

(2) Decreasing order of E.A.

(3) Decreasing order of Z_{eff}

(4) Decreasing order of size

28. Consider the following reactions:

(I) $O^{\ominus}(g) + e^- \longrightarrow O^{2-}(g), \Delta H_1$

(II) $F(g) + e^- \longrightarrow F^{\ominus}(g), \Delta H_2$

(III) $Cl(g) + e^- \longrightarrow Cl^{\ominus}(g), \Delta H_3$

(IV) $O(g) + e^- \longrightarrow O^{\ominus}(g), \Delta H_4$

Select the correct statements

(1) ΔH_4 is less negative than ΔH_2

(2) ΔH_3 is more negative than ΔH_2 and ΔH_4

(3) ΔH_3 and ΔH_4 are negative whereas ΔH_1 and ΔH_2 are positive

(4) ΔH_2, ΔH_3 and ΔH_4 are negative whereas ΔH_1 is positive

29. Consider the following sequence of reaction.

$$A^{\ominus} \xleftarrow{\Delta H_4} A \xrightarrow{\Delta H_1} A^{\oplus} \xrightarrow{\Delta H_2} A^{2+} \xrightarrow{\Delta H_3} A^{3+}$$

$$A^{\ominus} \xrightarrow{\Delta H_5} A \qquad A^{\oplus} \xrightarrow{\Delta H_6} A$$

If the electronic configuration of element A is $[Ne]3s^1$, then which of the following order is correct regarding given enthalpies?

(1) $|\Delta H_1| = |\Delta H_6|$ (2) $|\Delta H_2| = |\Delta H_1|$

(3) $|\Delta H_4| = |\Delta H_5|$ (4) $|\Delta H_2| = |\Delta H_3|$

Electronegativity (EN)

30. Which of the following properties can be determined by using Born–Haber cycle?

(1) $\Delta_{hyd}H^{\ominus}$ (2) $\Delta_{eg}H^{\ominus}$

(3) $\Delta_u H^{\ominus}$ (4) EN

31. Select the correct statement(s).

(1) On Mulliken scale, the average of IP and EA (in eV atom^{-1}) is known as EN.

(2) The maximum EN is shown by Cl.

(3) H, P and Te have similar value of EN.

(4) H, S and Te have similar value of EN.

32. Select the correct statement(s).

(1) Mulliken's values of EN are about 2.8 times more than the Pauling scale.

(2) Mulliken's values of EN are about 2.8 times less than the Pauling scale.

(3) On Mulliken's scale if IP and EA are in kJ mol^{-1}, then $EN = \dfrac{IP + EA}{540}$.

(4) On Mulliken's scale if IP and EA are in kcal mol^{-1}, then $EN = \dfrac{IP + EA}{2 \times 62.5}$.

33. Select the correct statement(s).

(1) On Pauling scale, the difference in EN of two atoms A and B in SI units is.

$(EN_A - EN_B) = 0.1017\sqrt{\Delta_{A-B}}$.

(2) On Pauling scale, the difference in EN of two atoms A and B in kcal mol^{-1} is

$(EN_A - EN_B) = 0.208\sqrt{\Delta_{A-B}}$.

(3) The Mulliken's EN values are scaled down to match the Pauling value by dividing $\left(\dfrac{IP + EA}{2}\right)$ in eV by 3.17.

(4) The Mulliken's EN values are scaled down to match the Pauling value by multiplying $\left(\dfrac{IP + EA}{2}\right)$ in eV by 3.17.

34. Select the correct statement(s).

(1) EN of Ga and Ge > EN of Al and Si, due to *d*-block contraction.

(2) EN of Ga and Ge < EN of Al and Si, due to *d*-block contraction.

(3) EN of Pb > EN of Tl and Bi, due to *d*-block contraction.

(4) EN of Pb < EN of Tl and Bi, due to *d*-block contraction.

35. Select the correct statements

(1) EN of Cl atom in Cl_2O_7 > EN of atom in Cl_2O_5

(2) EN of Cu^{2+} > EN of Cu^{2+}

(3) EN of C-atom in CH_4 > EN of C-atom in CO_2

(4) EN of atom on Pauling scale > EN of F atom on Mulliken scale

36. Select correct statement

(1) EN of Si atom using Allred-Rochow's method, if covalent radius of Si is 1.0Å is 3 (rounded in nearest integer value)

(2) EN of central atom $CF_4 > CH_4 > SiH_4$

(3) EN can not be determined using Born Haber cycle

(4) EN of central atom: $CF_4 > CCl_4 > CH_4$

37. Select the correct statements

(1) EN of an element $\propto Z_{eff}$

(2) EN of a cation $\propto$ Charge on cation

(3) EN $\propto$ s-character in hybrid orbital

(4) EN of a anion $\propto$ Charge on the anion

38. Which of the following elements have almost equal value of EN on Pauling scale.
(1) P
(2) S
(3) H
(4) Te

39. Select the correct statements
(1) $\Delta_{hydration} H^{\ominus} Mg^{2+} > \Delta_{hydration} H^{\ominus} Al^{+3}$
(2) $\Delta_{hydration} H^{\oplus}$ is maximum among $OH^{\ominus}$, $NH_4^{\oplus}$ and $F^{\ominus}$
(3) In the preparation of F_2, the strongest oxidizing halogen, the EA is the most important factor.
(4) $F^{\ominus}$ ion has highest hydrated radius among the other halide ions

40. Select the correct statements
(1) NaF has the highest melting point amongst NaF, NaCl, NaBr and NaI
(2) MgO has maximum lattice energy amongst MgO, CaO, BaO and SrO
(3) LiF has a positive enthalpy of solution amongst LiF, LiCl, LiBr and LiI
(4) KF has more negative enthalpy of solution amongst KF, KCl, KBr and KI

Miscellaneous

41. Transition metals are characterised by which of the following properties?
(1) Variable valency
(2) Coloured compounds
(3) High melting and boiling points
(4) Tendency to form complexes

42. Which is correct statement regarding BOH (where χ is electronegativity)?
(1) If $\chi_O - \chi_B > \chi_O - \chi_H$, BOH will be basic.
(2) If $\chi_O - \chi_B < \chi_O - \chi_H$, BOH will be acidic.
(3) If $\chi_O - \chi_B > \chi_O - \chi_H$, BOH will be acidic.
(4) If $\chi_O - \chi_B < \chi_O - \chi_H$, BOH will be basic.

43. The elements which are radioactive and have been named after the names of planet are
(1) Hg (Mercury) (Hergentium)
(2) Np (Neptunium)
(3) Pu (Plutonium)
(4) Ra (Radium)

44. The properties which are common to the elements belonging to groups 1 and 17 of periodic tables are
(1) Electropositive character increases down the group.
(2) Reactivity decreases from top to bottom.
(3) Atomic radii increase as atomic number increases.
(4) Electronegativity decreases on moving down a group.

45. The number of which subatomic particle is same in case of chlorine atom and chloride ion?
(1) Electron
(2) Proton
(3) Neutrons
(4) All of the above

46. Which of the following show amphoteric behaviour?
(1) $Zn(OH)_2$
(2) BeO
(3) Al_2O_3
(4) $Pb(OH)_2$

47. Which is correct in increasing order of ionic character?
(1) $AlCl_3 < MgCl_2 < NACl$
(2) $LiI < LiBr < LiCl < LiF$
(3) $NaCl > MgCl_2 < AlCl_3$
(4) None of the above

48. Highly pure dilute solution of sodium in ammonia
(1) Shows blue colouration due to solvated electrons
(2) Shows electrical conductivity due to both solvated electrons and solvated sodium ions
(3) Shows red colouration due to solvated electrons but bad conductor of electricity
(4) Produces hydrogen gas or carbonate

49. Which of the following are ionic carbides?
(1) CaC_2
(2) Al_4C_3
(3) SiC
(4) Be_2C

50. Which of the following substance(s) is/are used in laboratory for drying purposes?
(1) Anhydrous P_2O_5
(2) Graphite
(3) Anhydrous $CaCl_2$
(4) Na_3PO_4

51. Born–Haber cycle cannot be used to estimate
(1) Electronegativity
(2) Hydration energy
(3) Lattice energy of ionic crystals
(4) Binding energy of electrons

52. The compound(s) which have – O – O – bond(s) is/are
(1) BaO_2
(2) Na_2O_2
(3) CrO_5
(4) Fe_2O_3

53. Which of the following compounds are paramagnetic in nature?
(1) KO_2
(2) K_2O_2
(3) Na_2O_2
(4) RbO_2

54. Select the correct statement(s).
(1) Cr^{2+} compounds are ionic.
(2) They are oxidised to Cr^{3+} by air.
(3) They are reducing agent in aqueous solution.
(4) None is correct.

55. On moving down the group from F to I, which of the following properties decreases?
(1) Ionic radius
(2) IE
(3) Oxidising power
(4) EN

56. Select the correct statement(s).
(1) Alkali metals have lowest IE in respective period.
(2) Noble gas have highest IE is respective period.
(3) EA_1 of N < EA_1 of O.
(4) $F^{\ominus}$ is the strongest reducing agent among halide ions.

57. The electronic configuration of given species (X) is $1s^2, 2s^2, 2p^6, 3s^2\, 3p^6\, 3d^5, 4s^1$. This can be its
(1) Cationic form $X^{\oplus}$
(2) Anionic form $X^{\ominus}$
(3) Excited state
(4) Ground state

58. Which of the following sets contain only isoelectronic species?
(1) $K^{\oplus}, Ca^{2+}, Sc^{3+}, Cl^{\ominus}$
(2) $Zn^{2+}, Ca^{2+}, Ga^{3+}, Al^{3+}$
(3) Ti, Ar, Cr^{6+}, V^{5+}
(4) $P^{3-}, S^{2-}, Cl^{\ominus}, K^{\oplus}$

59. In which of the following arrangements, the order is according to the property indicated against it?
(1) IE_1: O > N > C > B
(2) $\Delta_{eg}H^{\oplus}$ (with –ve sign): Cl > F > Br > I
(3) Metallic radius: Rb > K > Na > Li
(4) Ionic size: $F^{\ominus} > Na^{\oplus} > Mg^{2+} > Al^{3+}$

60. In which of the following arrangements, the order is according to the property indicated against it?
(1) Basic strength: $SbH_3 > AsH_3 > PH_3 > NH_3$
(2) IE_1: N > O > C > B.
(3) Oxidising power: $PbO_2 > SnO_2 > SiO_2 > CO_2$
(4) Acid strength: HI > HBr > HCl > HF

61. The bond dissociation energy of B–F in BF_3 is 646 kJ mol^{-1} whereas that of C–F in CF_4 is 515 kJ mol^{-1}. The correct reason for higher B–F bond dissociation energy as compared to that of C–F in CF_4 is
(1) Lower degree of $p\pi$–$p\pi$ interaction between B and F in BF_3 than that between C and F in CF_4
(2) Significant $p\pi$–$p\pi$ interaction between B and F in BF_3 whereas there is no possibility of such interaction between C and F in CF_4
(3) Smaller size of B-atoms as compared to that of C-atom and the stronger bond between B and F in BF_3 as compared to that between C and F in CF_4
(4) Lewis acid character of boron trihalides is as: $BBr_3 > BCl_3 > BF_3$

62. Which of the following can conduct electricity in?
(1) $MgBr_2$ (2) $CaBr_2$
(3) $BaBr_2$ (4) $BeBr_2$

63. Which of the following are expected to be covalent?
(1) $BeCl_2$ (2) $SnCl_4$
(3) CuS (4) $CaCl_2$

64. Which of the following does not exist?
(1) HS_6 (2) HPO_4
(3) FeI_3 (4) $HClO_4$

65. Which of the following relation is/are correct?
(1) Covalent character $\propto$ Pseudo inert configuration
(2) Ionic character $\propto$ Inert configuration
(3) Covalent character $\propto \dfrac{1}{\text{Dipole moment}}$
(4) Ionic character $\propto \dfrac{1}{\text{Dipole moment}}$

66. Which of the following are correct?
(1) As^{5+} salts are better oxidising agents
(2) Tl^{3+} salts are better oxidising agents
(3) $Ga^{\oplus}$ salts are better reducing agents
(4) Pb^{4+} salts are better oxidising agents

Linked Comprehension Type

Paragraph 1

Effective nuclear charge (Z_{eff}) is the net attractive force on electrons under consideration and is equal to:

$Z_{eff} = Z - \sigma$ (nuclear charge – screening constant). Z_{eff} or σ is calculated by Slater's formuls, as given.

If one electron is present in the outermost orbit, there will be no screening in that orbital. Each electron contribute, 0.35 (total electrons minus one electron) present in the outermost shell.

A contribution of 0.85 for each electron is taken in the $(n - 1)$th shell.

1. The screening constant (σ) for 4*s* electron of Mn ($Z = 25$) will be
(1) 18.00 (2) 4.25
(3) 18.35 (4) 22.6

2. Which of the following statement is wrong?
(1) IE_1 of Ga > Al, due to imperfect shielding of 3*d*-orbitals in Ga.
(2) IE_1 of Ga < Al, due to perfect shielding of 3 *d*-orbitals in Ga.
(3) The atomic size of Ga and Al are almost same because of poor shielding effect of electrons in *d*-orbitals as the effective nuclear charge increases in Ga.
(4) IE_1 of group 16 elements is less than that of group 15 elements.

3. Which of the following statement is wrong?
(1) The number of lobes in *f*-orbitals are 8.
(2) IE_1 of elements increases along the period.
(3) IE_1 of the group 3 elements is more than that of the group 2 elements.
(4) IE_1, IE_2 and IE_3 of an element are 9.5, 18.5 and 154.4 eV. Predict that the element has either two *s*-electrons or two *p*-electrons in the valence shell.

Paragraph 2

In the long or modern form of the periodic table, the elements in the periodic table have been divided into four blocks, *s*-, *p*-, *d*-, and *f*-. Each period begins with the filling of new energy shell. Two series of *f*-block elements are placed at the bottom of the periodic table.

4. The element with $Z = 39$ belongs to
(1) *s*-block (2) *p*-block
(3) *d*-block (4) *f*-block

5. The element with $Z = 113$ has been discovered. Its block, group number, period and ourershell electronic configuration are
(1) *s*-block, group 2, period 7, $7s^2$
(2) *p*-block, group13, period 7, $7s^2\,7p^1$
(3) *p*-block, group13, period 6, $6s^2\,6p^1$
(4) *d*-block, group 12, period 6, $5d^{10}$, $6s^2$

6. Which of the element whose atomic numbers are given below cannot be accommodated in the present set-up of the modern periodic table?
(1) 109 (2) 118
(3) 120 (4) 125

7. What is the maximum number of electrons that can be accommodated with $n = 5$ (n = principal quantum number)?
(1) 10 (2) 18
(3) 36 (4) 54

8. Which of the following ions is most stable?
(1) $Li^{\ominus}$ (2) $Be^{\ominus}$
(3) $B^{\ominus}$ (4) $C^{\ominus}$

9. The last element of the *p*-block in the present periodic table is represented by the configuration, where [X] represents inert gas is
(1) [X] $7s^2\,7p^6$ (2) [X] $5f^{14}, 6d^{10}, 7s^2\,7p^5$
(3) $[X]4f^{14}, 5d^{10}, 6s^2\,6p^6$ (4) [X] None of the above

10. If the elements were discovered in future in which the electrons would be present in *g*-orbitals. Then *g*-orbital starts and ends up with what atomic number?
(1) 121, 139 (2) 121, 138
(3) 122, 140 (4) 122, 139

Paragraph 3

The energy required to remove an electron from the outermost shell of an isolated gaseous atom is known as IE_1 of that atom. Similarly, the energy required for the removal of the electron from the unipositive ion, diapositive ion and tripositive ion are known as IE_2, IE_3 and IE_4, respectively, and are called successive ionisation energies. The magnitude of the charge depends on the size of the orbital of electron. Electrons in smaller orbitals are on average close with each other and have more repulsion. Thus for Be ($2s^2$), the IE_1 and IE_2 are 9.3 and 18.2 eV atom^{-1}, whereas for Ca ($4s^2$), the values are 6.1 and 11.9 eV.

11. The correct order of arrangement of the first ionisation energies of C, N, O and F (in decreasing values) is
(1) C > N > O > F (2) O > N > F > C
(3) O > F > N > C (4) F > N > O > C

12. Four elements have the following first ionization energies in kJmol^{-1}: 762, 709, 59 and 558. The elements are Ga, Ge, In and Sn (not in order). Which of these elements has the ionisation energy of 762 kJmol^{-1}?
(1) In (2) Ga
(3) Sn (4) Ge

13. Which of the following are isoelectronic species?
$$1 \rightarrow CH_3^{\oplus}, II \rightarrow NH_2^{\ominus}, III \rightarrow NH_4^{\oplus}, IV \rightarrow NH_3$$
(1) I, II and III (2) II, III and IV
(3) I, II and IV (4) II and I

14. Among the following ionisation reactions, which one will have the maximum value of ionisation energy?
(1) $Be \rightarrow Be^{\oplus}$ (2) $Be^{\oplus} \rightarrow Be^{2+}$
(3) $Sr \rightarrow Sr^{\oplus}$ (4) $Sr^{\oplus} \rightarrow Sr^{2+}$

15. Consider the IE_1 of the elements whose electronic configurations correspond to the following:
i. [He] $2s^2\,2p^3$ **ii.** [He] $2s^2\,2p^4$
iii. [Ne] $3s^2\,3p^1$ **iv.** [Ar] $3d^{10}\,3s^2\,3p^1$
Which of the above have almost same IE_1?
(1) i and ii (2) i and iii
(3) iii and iv (4) ii and iv

16. The relationship between IE_4 and IE_2 of an element is
(1) $IE_4 > IE_2$ (2) $IE_4 < IE_2$
(3) $IE_4 = IE_2$ (4) None of the above

Paragraph 4

Energy is released when an electron is added to neutral isola[ted] gaseous atom in its ground state to give monoanion and th[e] is known as EA, or $\Delta_{eg}H_1^{\ominus}$. The greater the amount of ene[rgy] released the greater is the EA. EA is expressed in eV atom^{-1} [or] kcal or kJ mol^{-1}.

17. The EA values of elements depends on the following:
i. Nuclear charge
ii. Electronic configuration
iii. Atomic size
iv. Chemical environment
(1) i, iii, iv (2) i, ii, iii
(3) ii, iii, iv (4) All

18. EA values of N and P are exceptionally low, because
(1) Both N and P have half-filled *p*-orbitals in the valen[ce] shell.
(2) The atom is more stable than the corresponding anion.
(3) The electronic configuration of the anion $N^{\ominus}$ and $P^{\ominus}$ [is] relatively more stable than the corresponding atom.
(4) Both (2) and (3).

19. Select the correct statements (more than one correct).
(1) EA and $\Delta_{eg}H_1^{\ominus}$ of an atom of element have same magnitude
(2) $\Delta_{eg}H_1^{\ominus}$ of Al > B
(3) $\Delta_{eg}H_1^{\ominus}$ of P > N
(4) $\Delta_{eg}H_1^{\ominus}$ of S > O

20. Select the correct statements (more than one correct).
(1) $\Delta_{eg}H^{\ominus}$ of noble gases have large positive values.
(2) $\Delta_{eg}H^{\ominus}$ of noble gases have large negative values.
(3) $\Delta_{eg}H^{\ominus}$ of helium (He) is the lowest of all the noble gases.
(4) $\Delta_{eg}H^{\ominus}$ of Ar is lower than that of Ne.

Paragraph 5

Along the period (→) atomic/ionic radii and metallic character decreases while IE, EN, non-metallic character and oxidising power increases. Down the group (↓), atomic/ionic radii, metallic character and reducing character increase while IE and EN decrease. However, $\Delta_{eg}H^{\ominus}$ becomes less negative down a group but more negative along a period.

21. Which of the following isoelectronic species has lowest IE_1?
(1) $K^{\oplus}$ (2) Ca^{2+}
(3) S^{2-} (4) $Cl^{\ominus}$

22. If the ionic radii of $M^{\oplus}$ and $X^{\ominus}$ are about 135 pm, the expected values of metallic radii of M and X should be respectively.
(1) 65 and 230 pm (2) 230 and 60 pm
(3) 230 and 135 pm (4) 135 and 135 pm

23. In which of the following pairs, both species have nearly the same size? (more than one correct)
(1) Mg^{2+}, Al^{3+} (2) $K^{\oplus}, F^{\ominus}$
(3) $Li^{\oplus}, Mg^{2+}$ (4) $Rb^{\oplus}, O^{2-}$

24. Correct order of IE_2 of the following is
(1) $F > O > N > C$ (2) $O > N > F > C$
(3) $O > F > N > C$ (4) $C > N > O > F$.

25. Which of the following are correct statements? (more than one correct)
(1) IE and EA are defined at absolute zero temperature. At any other temperature, heat capacities for the reactants and products have to be taken into account.
(2) The ionisation enthalpy ($\Delta_i H^\ominus$) and IE are related to each other by the equation.
$\Delta_i H^\ominus$(ionisation enthalpy) = [IE (ionisation energy $+\frac{5}{2}RT$]
(3) The electron gain enthalpy ($\Delta_{eg} H^\ominus$) and EA are related to each other by the equation:
$\Delta_{eg} H^\ominus$(electron gain enthalpy) = [(–EA (electron affinity $-\frac{5}{2}RT$]
(4) The value of C_p (heat capacity at constant pressure and C_v (heat capacity at constant volume) are $\frac{3}{2}R$ and $\frac{5}{2}R$ respectively)

Matrix Match Type

1. Match the following statements with law and their discoverer.

	Statement		Law		Discoverer
(a)	Middle element of each of triads had an atomic weight half way between the atomic weights of the other two.	(i)	Law of triads	(p)	de Chancourtois
(b)	Arrangement of known elements in order of increasing atomic weights in a cylindrical table of elements to display the periodic recurrence of properties.	(ii)	Telluric screw or Helix law	(q)	Dobereiner
(c)	Arrangement of the lighter elements in increasing order of their atomic weights and noted that every eighth element had properties similar to the first element.	(iii)	Law of octaves	(r)	Newlands

2. Match the items given in Column I with that in the Column II.

	Column I Outer electronic configuration of element in ground state		Column II Characteristics period and group number
a.	$(n-2)f^1\ (n-1)d^1\ ns^2$	p.	6th period element
b.	$(n-1)d^5\ ns^1$	q.	Highest spin magnetic moment
c.	$ns^2\ np^3$	r.	Symmetrical distribution of electron density
d.	$(n-1)d^1ns^2$	s.	Period number is double than group number
		t.	Period number and group number are same.

3. Match the items given in Column I with that in the Column II.

	Column I Element (Electrons in K, L, M, N, ...)		Column II Characteristics
a.	A(2, 8, 7)	p.	Paramagnetic
b.	B(2, 8, 18, 8)	q.	3rd group element
c.	C(2,8,14,2)	r.	Last electron does not enter to valence shell
d.	D(2, 8,18, 25, 8, 2)	s.	Reactive non metal
		t.	Diamagnetic

4. Match the items given in Column I with that in the Column II.

	Column I (Electronic configuration)		Column II (Corresponding elements)
a.	[Xe] $4f^{14}\ 5d^2\ 6s^2$	p.	Inner-transition element
b.	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^6\ 7s^2$	q.	Representative element
c.	[Rn] $5f^{14}\ 6d^1\ 7s^2$	r.	d-block element
d.	[Xe] $4f^{14}\ 5d^{10}\ 6s^2$	s.	Transition element
		t.	*s*-block element

5. Match the items given in Column I with that in the Column II.

	Column I		Column II
a.	$Cr^{6+} > Cr^{3+} > Cr^{2+}$	p.	Hydration energy
b.	$K^\oplus > Na^\oplus > Li^\oplus$	q.	Hydrated size
c.	$Al^{+3} > Mg^{2+} > Na^\oplus$	r.	Ionic mobility
d.	$F^\ominus > Cl^\ominus > Br^\ominus > I^\ominus$	s.	Electrical conductance
		t.	Ionic radius

6. Match the items given in Column I with that in the Column II.

	Column I		Column II
a.	$\chi_{Pauling} = \frac{\chi_{Mulliken}}{y}$	p.	Alfred–Rochow scale
b.	$\chi_A = 0.744 + \frac{0.359\, Z_{eff}}{r^2}$	q.	Mulliken scale
c.	$\chi_A = \frac{(IP)_A + (EA)_A}{540}$ kJ mol^{-1}	r.	$y = 2.8$
d.	$\chi_A - \chi_B = 0.1017\,(\Delta_{A-B})^{\frac{1}{2}}$ (where Δ_{A-B} is in kJ mol^{-1}) $= E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$	s.	Pauling scale
		t.	$y = 1.4$

7. Match the items given in Column I with that in the Column II.

	Column I		Column II
a.	Covalent radius	p.	Diatomic molecule
b.	Crystal radius	q.	Halogens
c.	Leonard radius	r.	Metals
d.	van der Waals radius	s.	Inert gases

8. Match the items given in Column I with that in the Column II.

	Column I		Column II
a.	Na > Mg > Al > B	p.	Oxidising nature
b.	F > N > C > B > Si	q.	Lowest IE_1
c.	F > O > Cl > N	r.	Metallic character
d.	Out of B, C Al and SiC have	s.	Non-metallic
		t.	Hightest IE_1

9. Match the items given in Column I with that in the Column II.

	Column I		Column II
a.	N_2O	p.	Normal oxide
b.	Na_2O	q.	Neutral oxide
c.	Ga_2O_3	r.	Suboxide
d.	C_3O_2	s.	Basic oxide
e.	Mn_3O_4	t.	Amphoteric oxide
f.	SnO_2	u.	Mixed oxide

10. Match the items given in Column I with that in the Column II.

	Column I Ions		Column II Soft and hard acids and bases
a.	$Li^{\oplus}$, Mg^{2+}, Al^{3+}	p.	Soft acids
b.	$Cu^{\oplus}$, Cd^{2+}, Pt^{4+}	q.	Soft bases
c.	$\overset{\ominus}{O}H$, $NO_3^{\ominus}$, CO_3^{2-}	r.	Hard acids
d.	$H^{\ominus}$, $I^{\ominus}$, $CN^{\ominus}$	s.	Hard bases

11. Match the items given in Column I with that in the Column II.

	Column I Property		Column II Soft and hard acids and bases
a.	High electronegativity and low polarisability	p.	Soft bases
b.	Low electronegativety and high polarisability	q.	Hard bases
c.	Small size with high positive oxidation state	r.	Soft acids
d.	Large size with zero or low positive oxidation state	s.	Hard acids

12. Match the items given in Column I with that in Column II and III.

	Column I		Column II		Column III
a.	Anomalous pairs,	i.	Atomic masses	p.	Li, Mg;
b.	Diagonal relationship element pairs	ii.	K, Ar; Co, Ni	q.	Li,Na; Be, Mg
c.	Lother Meyer graph shows a relation between	iii.	Be, Al; B, Si	r.	Zn, Cd; Hg, Uub
d.	Typical elements	iv.	B, Al; C, Si	s.	Te, I; Th, Pa
e.	In second group, Mg acts as a bridge element. The properties of bridge element are somewhat mixed properties of elements of two sub groups as Mg shows similarities with them	v	Ca, Sr; Ba, Ra	t.	Atomic volumes

13. Match the items given in Column I with that in Column II and III.

	Column I		Column II		Column III
a.	IA	i.	Liquid metal	p.	Halogen
b.	*d*-block element	ii.	Liquid non-metal	q.	$3s^2\ 3p^4$
c.	mercury	iii.	Diamond	r.	ns^1
d.	Bromine	iv.	VIA group	s.	Variable valency
e.	Carbon	v.	Alkali metals	t.	Coinage metal
f.	Sulphur	vi.	Noble metal	u.	Amalgam
g.	Gold	vii.	Transition metals	v.	Hardest substance

Numerical Value Type

1. Among the following oxides how many of them are suboxides?
   a. C_3O_2 b. N_2O
   c. NO_2 d. CO
   e. Fe_3O_4 f. KO_2
2. The number of factors that influence the IE are
   a. Size of the atom b. Charge on the nucleus
   c. Shielding effect d. The atomic mass
3. The number of process(es) requiring the absorption of energy is/are
   a. $Cl \longrightarrow Cl^{\ominus}$ b. $O^{\ominus} \longrightarrow O^{2-}$
   c. $Fe^{+3} \longrightarrow Fe^{+2}$ d. $Ar \longrightarrow Ar^{\ominus}$
4. For an element (X) the successive ionisation energies, IE_1, IE_2, IE_3, IE_4 and IE_5 are 800, 2427, 3658, 25024 and 32824 kJ mol^{-1} respectively, then what is the number of valence electrons present in the element?
5. The diagonal relationship is shown by the elements upto how many groups only?
6. The number of the following pairs contains elements with similar atomic radii
   a. Co, Ni b. Zn, Mo
   c. Rh, Ir d. Hf, Ti
7. How many of the following energies are involved in the transformation of $Na(s) \longrightarrow Na^{\oplus}(aq)$?
   a. IE b. $\Delta_{Sub}H^{\ominus}$
   c. $\Delta_{diss.}H^{\ominus}$ d. $\Delta_{hyd.}H^{\ominus}$
   e. $\Delta_u H^{\ominus}$
8. Among the following oxides how many of them are mixed oxides?
   a. H_2O b. C_3O_2 c. Fe_3O_4 d. Fe_2O_3
   e. Pb_3O_4 f. PbO_2 g. $Co(AlO_2)_2$ h. Mn_3O_4
9. Number of species that are isoelectronic with Ar is.
10. Among the following oxides, how many of them are amphoteric oxides?
    a. B_2O_3 b. Al_2O_3 c. CaO d. ZnO
    e. Ga_2O_3 f. SnO_2 g. PbO_2 h. BeO
    i. CuO j. Fe_2O_3
11. Among the following elements how many of them are inner transition elements?
    a. Sg b. Bk c. Er d. Em
    e. Fe f. Pb g. Cr h. Ca
    i. Ar j. Zr k. Ce
12. How many number of pairs of elements exhibit diagonal relationship.
13. Among $BeCO_3$, $CaCO_3$, $SrCO_3$ and $BaCO_3$, how many number of these compounds are thermally more stable than $MgCO_3$?
14. On the basis of quantum number, which period of the periodic table should have 32 elements.
15. What is the atomic number of the element present in the second period and group 15.
16. $\Delta_f H^{\ominus}$ of hypothetical *MX* is –150 kJ mol^{-1} and for MX_2 is – 600 kJ mol^{-1}. The enthalpy of disproportionation of *MX* is = – 100 *x* kJ mol^{-1}.
    Find the value of *x*.
17. If heat of solution for XY(s) is -0.8×10^x kcal mol^{-1} and lattice energy for XY(s) is 700 kcal mol^{-1} and hydration energy for $X^{\oplus}(g)$ is –1000 kcal mol^{-1} and for $Y^{\ominus}(g)$ is –500 kcal mol^{-1} (g) then the value of *x* is:
18. Total number of representative elements in the given elements are:
    Mo, Pd, Po, Cd, Nb, Ta, Te, Ra, Te, At, Pb, Tl
19. Total number of elements which have only single oxidation state (other than zero) in their corresponding stable compounds.
    (1) B (2) Tl (3) Cs (4) F (5) Al
    (6) Zn (7) Ga (8) Pb (9) At (10) Fr
20. How many pairs are, in which 2nd species has lower ionization energy than first species.
    (a) Be and B (b) P and S (c) O and S
    (d) Br and K (e) N and O (f) Li and $Li^{\oplus}$
    (g) Ba and Sr (h) IE_2 of C and IE_2 of B
21. If value of spin quantum number(s) $= -\frac{1}{2}, 0, +\frac{1}{2}$
    Then number of groups in the new form of periodic table is: (If all other rules of electronic configuration are same)
22. An element 'A' has its electronic configuration of K shell is $(n-5)s^2$ and it has total number of electrons in its outer-most, penultimate and antipenultimate shell are 2, 8 and 23 respectively, then total number of electrons in element 'A' in its ground state are:

Archives

JEE MAIN

Single Correct Answer Type

1. The set representing the correct order of ionic radius is
   (1) $Li^+ > Be^{2+} > Na^+ > Mg^{2+}$
   (2) $Na^+ > Li^+ > Mg^{2+} > Be^{2+}$
   (3) $Li^{2+} > Na^+ > Mg^{2+} > Be^{2+}$
   (4) $Mg^{2+} > Be^{2+} > Li^+ > Na^+$ **(AIEEE 2009)**

2. The correct sequence which shows decreasing order of the ionic radii of the elements is
   (1) $Al^{3+} > Mg^{2+} > Na^+ > F^- > O^{2-}$
   (2) $Na^+ > Mg^{2+} > Al^{3+} > O^{2-} > F^+$
   (3) $Na^+ > F^- > Mg^{2+} > O^{2-} > Al^{3+}$
   (4) $O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$ **(AIEEE 2010)**

3. The correct order of electron gain enthalpy with negative sign of F, Cl, Br, and I, having atomic number 9, 17, 35, and 53 respectively, is
   (1) $I > Br > Cl > F$ (2) $F > Cl > Br > I$
   (3) $Cl > F > Br > I$ (4) $Br > Cl > I > F$
   (AIEEE 2011)

4. Which one of the following orders presents the correct sequence of the increasing basic nature of the given oxides?
   (1) $Al_2O_3 < MgO < Na_2O < K_2O$
   (2) $MgO < K_2O < Al_2O_3 < Na_2O$
   (3) $Na_2O < K_2O < MgO < Al_2O_3$
   (4) $K_2O < Na_2O < Al_2O_3 < MgO$ **(AIEEE 2011)**

5. The increasing order of the ionic radii of the given isoelectronic species is
   (1) Cl^-, Ca^{2+}, K^+, S^2 (2) $S^{2-}, Cl^-, Ca^{2+}, K^+$
   (3) $Ca^{2+}, K^+, Cl^+, S^{2-}$ (4) $K^+, S^{2-}, Ca^{2+}, Cl^-$
   (AIEEE 2012)

6. The first ionization potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be
   (1) –2.55 eV (2) –5.1 eV
   (3) –10.2 eV (4) +2.55 eV
   (JEE Main 2013)

7. Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se, and Ar?
   (1) $Ca < S < Ba < Se < Ar$ (2) $S < Se < Ca < Ba < Ar$
   (3) $Ba < Ca < Se < S < Ar$ (4) $Ca < Ba < S < Se < Ar$
   (JEE Main 2013)

8. The ionic radii (in Å) of N^{3-}, O^{2-} and F^- are respectively:
   (1) 1.36, 1.40 and 1.71 (2) 1.36, 1.71 and 1.40
   (3) 1.71, 1.40 and 1.36 (4) 1.71, 1.36 and 1.40
   (JEE Main 2015)

9. Which of the following atoms has the highest first ionization energy? **(JEE Main 2016)**
   (1) Sc (2) Rb
   (3) Na (4) K

10. In the following reactions, ZnO is respectively acting as a/an:
    (A) $ZnO + Na_2O \longrightarrow Na_2ZnO_2$
    (B) $ZnO + CO_2 \longrightarrow ZnCO_3$
    (1) base and acid (2) base and base
    (3) acid and acid (4) acid and base
    (JEE Main 2017)

11. The group having isoelectronic species is:
    (1) $O^{2-}, F^-, Na^+, Mg^{2+}$ (2) O^-, F^-, Na, Mg^+
    (3) O^{2-}, F^-, Na, Mg^{2+} (4) $O^- F^-, Na^+, Mg^{2+}$
    (JEE Main 2017)

JEE ADVANCED

Single Correct Answer Type

1. Which of the following represent the correct order of increasing IE_1 for Ca, Ba, S, Se and Ar?
   (1) $S < Se < Ca < Ba < Ar$ (2) $Ba < Ca < Se < S < Ar$
   (3) $Ca < Ba < S < Se < Ar$ (4) $Ca < S < Ba < Se < Ar$
   (JEE Advanced 2013)

Multiple Correct Answers Type

1. The option(s) with only amphoteric oxides is(are)
   (1) Cr_2O_3, BeO, SnO, SnO_2 (2) Cr_2O_3, CrO, SnO, PbO
   (3) NO, B_2O_3, PbO, SnO_2 (4) ZnO, Al_2O_3, PbO, PbO_2
   (JEE Advanced 2017)

Answers Key

EXERCISES

Single Correct Answer Type

1. (2)	2. (1)	3. (1)	4. (3)	5. (4)
6. (4)	7. (3)	8. (2)	9. (3)	10. (4)
11. (3)	12. (4)	13. (1)	14. (3)	15. (3)
16. (1)	17. (3)	18. (2)	19. (2)	20. (1)
21. (4)	22. (3)	23. (1)	24. (4)	25. (2)
26. (1)	27. (4)	28. (3)	29. (1)	30. (4)

31. (3)	**32.** (1)	**33.** (4)	**34.** (2)	**35.** (4)
36. (2)	**37.** (1)	**38.** (4)	**39.** (2)	**40.** (3)
41. (4)	**42.** (1)	**43.** (3)	**44.** (1)	**45.** (2)
46. (1)	**47.** (3)	**48.** (3)	**49.** (4)	**50.** (4)
51. (1)	**52.** (4)	**53.** (3)	**54.** (4)	**55.** (1)
56. (4)	**57.** (3)	**58.** (2)	**59.** (2)	**60.** (2)
61. (2)	**62.** (4)	**63.** (2)	**64.** (2)	**65.** (3)
66. (3)	**67.** (1)	**68.** (4)	**69.** (2)	**70.** (3)
71. (2)	**72.** (3)	**73.** (4)	**74.** (4)	**75.** (2)
76. (2)	**77.** (4)	**78.** (3)	**79.** (4)	**80.** (1)
81. (3)	**82.** (2)	**83.** (3)	**84.** (1)	**85.** (1)
86. (4)	**87.** (4)	**88.** (3)	**89.** (1)	**90.** (3)
91. (1)	**92.** (4)	**93.** (3)	**94.** (1)	**95.** (4)
96. (1)	**97.** (3)	**98.** (2)	**99.** (2)	**100.** (3)
101. (1)	**102.** (1)	**103.** (4)	**104.** (2)	**105.** (3)
106. (3)	**107.** (2)	**108.** (3)	**109.** (1)	**110.** (3)
111. (3)	**112.** (1)	**113.** (3)	**114.** (4)	**115.** (3)
116. (1)	**117.** (3)	**118.** (2)	**119.** (2)	**120.** (1)
121. (2)	**122.** (1)	**123.** (4)	**124.** (4)	**125.** (2)
126. (1)	**127.** (1)	**128.** (1)	**129.** (1)	**130.** (2)
131. (4)	**132.** (2)	**133.** (3)	**134.** (1)	**135.** (4)
136. (4)	**137.** (2)	**138.** (4)	**139.** (1)	**140.** (1)
141. (2)	**142.** (3)	**143.** (4)	**144.** (2)	**145.** (1)
146. (2)	**147.** (1)	**148.** (1)	**149.** (4)	**150.** (2)
151. (1)	**152.** (1)	**153.** (3)	**154.** (1)	**155.** (2)
156. (2)	**157.** (4)	**158.** (1)	**159.** (1)	**160.** (2)
161. (3)	**162.** (1)	**163.** (3)	**164.** (1)	**165.** (4)
166. (3)	**167.** (3)	**168.** (2)	**169.** (3)	**170.** (3)
171. (2)	**172.** (3)	**173.** (4)	**174.** (3)	**175.** (1)
176. (3)	**177.** (1)	**178.** (3)	**179.** (4)	**180.** (3)
181. (2)				

Multiple Correct Answers Type

1. (2, 3, 4)	**2.** (1, 2, 3, 4)	**3.** (3, 4)
4. (3,4)	**5.** (1, 2)	**6.** (1, 2, 4)
7. (1, 3, 4)	**8.** (1, 2, 3, 4)	**9.** (1, 3)
10. (1, 2, 4)	**11.** (1, 2, 3, 4)	**12.** (1, 2, 3)
13. (1, 4)	**14.** (3, 4)	**15.** (1, 2, 3)
16. (1, 4)	**17.** (1, 3)	**18.** (2, 3)
19. (1, 2)	**20.** (3)	**21.** (1, 2, 3)
22. (1, 2, 3)	**23.** (1, 2, 4)	**24.** (1, 3)
25. (1, 2, 3)	**26.** (1, 2, 3)	**27.** (1,2,3)
28. (1, 2, 4)	**29.** (1, 2, 3)	**30.** (2, 3)
31. (1, 3)	**32.** (1, 3, 4)	**33.** (1, 2, 3)
34. (1, 3)	**35.** (1, 2)	**36.** (2, 3, 4)
37. (1, 2, 3)	**38.** (1, 3, 4)	**39.** (2, 4)
40. (1, 2, 3, 4)	**41.** (1, 2, 3, 4)	**42.** (1, 2)
43. (2, 3)	**44.** (1, 3, 4)	**45.** (2, 3)
46. (1, 2, 3, 4)	**47.** (1, 2)	**48.** (1, 2)
49. (1, 2, 4)	**50.** (1, 3)	**51.** (1, 2, 4)
52. (1, 2, 3)	**53.** (1, 4)	**54.** (1, 2, 3)
55. (2, 3, 4)	**56.** (1, 2, 3)	**57.** (1, 4)
58. (1, 3, 4)	**59.** (2, 3, 4)	**60.** (2, 3, 4)
61. (2, 4)	**62.** (1, 2, 3)	**63.** (1, 2)
64. (1, 2, 3)	**65.** (1, 2, 3)	**66.** (2, 3, 4)

Linked Comprehension Type

1. (4)	**2.** (2)	**3.** (3)	**4.** (3)	**5.** (2)
6. (4)	**7.** (4)	**8.** (1)	**9.** (3)	**10.** (2)
11. (4)	**12.** (4)	**13.** (2)	**14.** (2)	**15.** (3)
16. (1)	**17.** (2)	**18.** (1)	**19.** (1, 2, 3, 4)	
20. (1, 2, 3)	**21.** (3)	**22.** (2)	**23.** (2, 3, 4)	
24. (3)	**25.** (1, 2, 3)			

Matrix Match Type

S.No.	a	b	c	d	e	f	g
1.	i, q	ii, p	ii, r				
2.	p, s	p, q, r, t	p, r	p, s			
3.	p, s	t	p, r	p, q, r			
4.	r, s	q, t	p	r			
5.	p, q, s	r, s, t	p, q, s	p, q			
6.	r	p	q	s			
7.	q	r	s	p			
8.	r	s	p	t			
9.	q, r	p, s	t	r			
10.	r	p	s	q			
11.	q, s	p, r	s	r			
12.	ii, s	ii, p	i, t	iv, q	v, r		
13.	v, r	vii, s	i, u	ii, p	ii, v	iv, q	vi, t

Numerical Value Type

1. (2)	**2.** (3)	**3.** (2)	**4.** (3)	**5.** (4)
6. (1)	**7.** (3)	**8.** (4)	**9.** (5)	**10.** (6)
11. (4)	**12.** (3)	**13.** (1)	**14.** (6)	**15.** (7)
16. (3)	**17.** (1)	**18.** (6)	**19.** (6)	**20.** (5)
21. (27)	**22.** (5)			

ARCHIVES

JEE Main

Single Correct Answer Type

1. (2)	**2.** (4)	**3.** (3)	**4.** (1)	**5.** (3)
6. (2)	**7.** (3)	**8.** (3)	**9.** (1)	**10.** (4)
11. (1)				

JEE Advanced

Single Correct Answer Type

1. (2)

Multiple Correct Answers Type

1. (1, 4)

2 Chemical Bonding and Molecular Structure

OVERVIEW

1. Kössel was the first to give the mechanism of the formation of electropositive and electronegative ions and related the process to the attainment of noble gas configurations by the respective ions. Electrostatic attraction between ions is the cause for their stability. This gives the concept of *electrovalency*.
2. Lewis was the first to give the description of *covalent bonding* in terms of the sharing of electron pairs between atoms and related the process to the attainment of noble gas configurations by reacting atoms as a result of sharing of electrons. The Lewis dot symbols show the number of valence electrons of the atoms of a given element and the Lewis dot structures show the pictorial representations of bonding in molecules.
3. a. The bond formed as a result of the electrostatic attraction between the +ve and –ve ions was termed as *electrovalent* or *ionic bond. The electrovalence* is equal to the number of unit charge(s) on the ion.

   b. An ionic compound is a three-dimensional aggregation of the +ve and –ve ions in an ordered arrangement called the crystal lattice, which is stabilised by *enthalpy of lattice formation*.

   c. Ionic bonds are formed easily if:

      i. The atoms forming the cation have low IE.

      ii. The atoms forming the anion have high $\Delta_{eg}H^{\ominus}$ (i.e. electron gain enthalpy) or EA.

      iii. High (–ve) lattice enthalpy ($\Delta_U H^{\ominus}$) of the ionic crystal formed.

   d. Thus, $\Delta_U H^{\ominus} \propto$ Magnitude of charge i.e. high charge of cation and anion.

      $\propto$ Small cation and large anion.

   e. An ionic bond is formed if:

      i. $IE + \Delta_{eg}H^{\ominus} - \Delta_U H^{\ominus} < 0$

      (OR)

      ii. $\Delta_U H^{\ominus} + EA\,(\text{or}\ \Delta_{eg}H^{\ominus}) > IE$

      Net effect is the release of energy

   f. **Characteristics of ionic compounds:**

      i. Crystalline in nature.

      ii. High melting and boiling points.

      iii. Soluble in polar solvents.

      iv. Furnish ions in solutions.

      v. Ionic bond is non-rigid and non-directional and thus these compounds do not show space or stereo-isomerism.

      vi. Show isomorphism properties.
4. a. Gilbert N. Lewis proposed the idea of *covalent bond*. An association through sharing of electron pairs among atoms of different or of same kind is known as *covalent bond*.

   b. While a single covalent bond is formed by sharing of an electron pair between two atoms, multiple bonds result from the sharing of two or three electron pairs. Some bonded atoms have additional pairs of electrons which are not involved in bonding. These are called lone pairs of electrons. A Lewis dot structure shows the arrangement of bonded pairs and lone pairs around each atom in a molecule. Important parameters, associated with chemical bonds, such as bond length, bond angle, bond enthalpy, bond order and bond polarity have significant effect on the properties of compounds.

   c. **Characteristics of covalent compounds:**

      i. Generally, they exist as liquid or gases of low boiling points under the normal conditions of temperature and pressure.

      ii. Have relatively low melting and boiling points. (Exception: Diamond, SiC, SiO_2, which have giant three-dimensional structures.)

      iii. Generally, they have three types of crystal structures:
      - The crystal structures in which molecules are held by van der Waals forces, e.g. S_8, I_2 and P_2O_5 etc.
      - The crystal structures in which the crystals having separated lattice layers, e.g. graphite.
      - The crystal structures in which the crystals form giant molecules e.g. SiC and AlN.

      iv. Generally, they are insoluble in polar solvents (Exception: Alcohols and amines dissolve in water due to H-bonding.)

      v. Generally, they are bad conductors of electricity. (Exception: Graphite.)

vi. The covalent bonds are directional and rigid. Thus, they can show structural and space isomerism.

vii. They show molecular reactions.

5. **Coordinate or dative bond:** Perkins postulated the idea of coordinate bond formation in which lone pairs used for sharing are donated by one of the combining atoms, e.g. in the formation of $NH_4^{\oplus}$ ion, O_3 and H_2O_2 molecule.

The properties of coordinate compounds are intermediate between the properties of electrovalent and covalent compounds.

6. **Formal charge:**

$$\left.\begin{array}{l}\text{Formal charge}\\ \text{(FC) on an}\\ \text{atom in a Lewis}\\ \text{structure}\end{array}\right] = \left[\begin{array}{c}\text{No. of}\\ \text{valence } e^-\text{'s}\end{array}\right] - \left[\begin{array}{c}\text{No. of}\\ lp\ e^-\text{'s}\end{array}\right] - \frac{1}{2}\left[\begin{array}{c}\text{No. of}\\ \text{bonding } e^-\text{'s}\end{array}\right]$$

7. **Resonance structures:** A number of molecules and polyatomic ions cannot be described accurately by a single Lewis structure and a number of descriptions (representations) based on the same skeletal structure are written and these taken together represent the molecule or ion. This is a very important and extremely useful concept called **resonance.** The contributing structure or *canonical forms* taken together constitute the resonance hybrid which represents the molecule or ion. Some examples of resonance are explained in Section. 2.15

8. a. **Dipole moment (μ):** It is the vector sum of all the individual bond moments. Mathematically, $\mu = q \times d$, where q is the magnitude of partial charges and d is the distance between the centres of opposite charge.

If q is of the order of 10^{-10} esu and d is the order of 10^{-10} cm (1 Å) then μ is of the order of $10^{-10} \times 10^{-8} = 10^{-18}$ esu cm.

This quantity is known as one Debye (D).

$\therefore\quad 1\text{D} = 10^{-18}$ esu cm

If q is in coulomb and d is in metre (m), then μ is expressed in coulomb metre (C.m)

In SI units:

$1 \text{ esu} = 1.602 \times 10^{-19}\text{ C}/4.803 \times 10^{-10}$

$= 3.335 \times 10^{-10}\text{ C}$

and $1 \text{ Cm} = 10^{-2}\text{ m}$

$\therefore\ 1\text{D} = 10^{-18}\text{ esu Cm} \times (3.335 \times 10^{-10}\text{ C}) \times (10^{-2}\text{ m}) = 3.335 \times 10^{-30}\text{ Cm}$

b. **Application of dipole moment:**

i. In determining the polarity of bonds.

ii. In calculation of percentage ionic character.

$$\%\text{ ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{calculated}}} \times 100$$

iii. In determining the shape of molecules.

iv. Distinction between *cis* and *trans* isomers.

v. Distinction between *o*, *m*- and *p*-isomers.

9. **The valence shell electron pair repulsion (VSEPR) theory:**

The VSEPR model used for predicting the geometrical shapes of molecules is based on the assumption that electron pairs (lp) repel each other and, therefore, tend to remain as far apart as possible. According to this model, the molecular geometry is determined by repulsions between lone pairs and lone pairs; lone pairs and bonding pairs and bonding pairs and bonding pairs. The order of these repulsions being : lp–lp > lp–bp > bp–bp.

10. **Valence bond theory (VBT):** VBT was introduced by Heitler and London and developed further by Pauling and Slater.

The valence bond (VB) approach to covalent bonding is basically concerned with the energetics of covalent bond formation about which the Lewis and VSEPR models are silent. Basically, the VBT discusses bond formation in terms of overlap of orbitals. For example, the formation of the H_2 molecule from two hydrogen atoms involves the overlap of the 1*s* orbitals of the two H atoms which are singly occupied. It was found that the potential energy of the system gets lowered as the two H atoms come near to each other. At the equilibrium internuclear distance (bond distance) the energy touches a minimum. Any attempt to bring the nuclei still closer results in a sudden increase in energy and consequent destabilisation of the molecule. Because of orbital overlap the electron density between the nuclei increases which helps in bringing them closer. However, the actual bond enthalpy and bond length values are not obtained by overlap alone and other variables have to be taken into account.

11. a. **Overlapping of atomic orbitals (AO's):** When two atoms come close to each other, there is overlapping of AO's. The overlap may be +ve; –ve or zero depending upon the properties of overlapping of AO's.

b. **Types of overlapping and nature of covalent bonds:** The covalent bond may be classified into two types depending upon the types of overlapping, i.e. (i) sigma (σ) bond and (ii) pi (π) bond.

i. **Sigma bond:** It is formed by the end to end overlap of bonding orbitals along the internuclear axis. It can by formed by any one of the following types of combinations of AO's

- *s-s* overlapping
- *s-p* overlapping
- *p-p* overlapping

ii. **pi (π) bond:** It is formed by the sidewise overlapping of bonding orbitals. π bond between two atoms is formed in addition to a σ-bond. It is always present in the molecules containing multiple bond.

c. **Strength of σ- and π-bond:** In case of σ-bond, the overlapping of orbitals takes place to a larger extent whereas in case of π-bond, the overlapping of orbitals occurs to a smaller extent.

Hence the strength of σ-bond is greater than the strength of π-bond.

12. a. **Hybridisation of AO's:** The process of mixing of AO's belonging to the same atom of slightly different energies so that a redistribution of energy takes place between them resulting in the formation of new set of orbitals of equivalent energies and shape is called *Hybridisation.*

Pauling and Slater introdeced the idea of hybridisation in order to explain the characteristics of geometrical shapes of polyatomic molecules such as CH_4, NH_3 and H_2O.

b. **Types of hybridisation**

i. Involving *s* and *p* AO's:

- Diagonal or linear or *sp* hybridisation.
- Trigonal or planar or sp^2 hybridisation.
- Tetrahedral or sp^3 hybridisation.

sp, sp^2, sp^3 hybridisation of AO's of Be, B, C, N, and O are used to explain the formation and geometrical shapes of molecules such as $BeCl_2$, BCl_3, CH_4, NH_3 and H_2O. They also explain the formation of multiple bonds in molecules such as C_2H_4 (ethene) and C_2H_2 (ethyne).

ii. Involving *s*, *p* and *d* AO's: The energies of 3*d* orbitals are comparable to the energies of the 3*s* and 3*p* orbitals and also to those of 4*s* and 4*p* orbitals. As a consequence, the hybridisation involving either 3*s*, 3*p* and 3*d* or 3*d*, 4*s* and 4*p* is possible. However, since the difference in energies of 3*p* and 4*s* orbitals is significant, no hybridisation involving 3*p*, 3*d* and 4*s* orbitals is possible.

The possible hybridisation involving *d*-orbitals are as follows:

- dsp^2
- sp^3d or dsp^3
- sp^3d^2 or d^2sp^3
- sp^3d^3 or d^3sp^3
- sp^3d^4 or d^4sp^3
- d^5sp^3.

Note: i. Summary of hybridisation, geometry and shapes of various molecules are given in Section 2.21.12.

ii. Some rules for predicting hybridisation and shapes of molecules/ions, refer to Section 2.21.9.

13. **Hydrogen bond:** H-bond is formed when an H-atom is in between two highly EN, and small atoms such as O, F and N. There are two types of H-bonds.

a. **Intermolecular H-bonding:** It exists between two or more molecules of the same or different substances, e.g. HF, H_2O, ROH (same molecule), and water and alcohol, ammonia and water (different compounds), etc.

For the consequence of intermolecular H-bonding, refer to Section 2.23.11.

i. Such compounds show abnormally high m.pt. and b.pt. e.g.

m.pt.	$\Rightarrow H_2O > NH_3 > HF$	b.pt.	$\Rightarrow H_2O > HF > NH_3$
	$\Rightarrow NH_3 > SbH_3 > AsH_3 > PH_3$		$\Rightarrow BiH_3 > SbH_3 > NH_3 > AsH_3 > PH_3$
	$\Rightarrow H_2O > H_2Te > H_2Se > H_2S$		$\Rightarrow H_2O > H_2Te > H_2Se > H_2S$
	$\Rightarrow HI > HF > HBr > HCl$		$\Rightarrow HF > HI > HBr > HCl$

ii. Such compounds are soluble in H_2O, e.g. lower alcohols and NH_3 are soluble in H_2O.

iii. Such compounds show high viscosity and high surface tension.

iv. They are less volatile.

b. **Intramolecular H-bonding:** This type of H-bonding occurs when polar H and EN atom are present in the same molecule.

c. **Consequence of intramolecular H-bonding:** This type of H-bonding decreases m.pt. and b.pt. and as well as their solubility in H_2O. For example, *o*-chlorophenol, *o*-nitrophenol and other *o*-derivatives show low m.pt. and b.pt. as compared to their *m*-or *p*-isomers. Similarly, *o*-nitrophenol and *o*-hydroxy benzaldehyde as soluble in hot water whereas their *m*- or *p*-isomers are soluble in cold water.

14. **Molecular orbital theory (MOT):**

a. VBT does not explain the following:

i. The formation of chemical bond of molecules.

ii. The relative bond strength.

iii. The magnetic and optical characteristics (i.e. colour) of molecules in visible light.

The above limitations of VBT were overcome by MOT, developed by F. Hund and R.S. Mulliken in 1932.

b. The salient features of this theory are as follows:

i. The AO's of comparable energies and proper symmetry combine. They lose their identity to form MO's.

For example, 1*s* can combine with 1*s* and with 2*s*. Similarly, *s* orbital can combine with p_z but not with p_x or p_y. Likewise p_z can combine with p_z but not with p_x or p_y.

ii. AO is monocentric while MO is polycentric.

iii. The number of MO formed is equal to the number of combining AO's. When two AO's combine, two MO's are formed (bonding MO and antibonding M.O). The bonding M.O's are represented by σ, π, δ etc. while the corresponding antibonding MO's are represented by σ*, π*, δ* etc.

iv. The bonding MO has lower energy and has greater stability than the corresponding antibonding MO.

v. Like AO's, MO's are filled in accordance with Aufbau rule obeying the Pauli's exclusion principle and Hund's rule.

vi. According to the principle of linear combination of atomic orbitals (LCAO), when two waves are in phase, they add up. When two are out of phase, they are subtracted from each other.

The MO (σ) formed by the additive effect of the AO's is called bonding MO and formed by the subtractive effect of the two AO's is called antibonding MO.

vii. The electron density in a bonding MO is located between the nuclei of the bonded atoms while in antibonding MO is located away from the space between the nuclei.

c. **Energy level diagram for MO's:** $1s$ AO's on two atoms form two MO's (σ $1s$ and σ^* $1s$). In the same manner, the $2s$ and $2p$ AO's (8 AO's on 2 atoms) give rise to the following 8 MO's.

Antibonding MO's	σ^*2s,	σ^*2p_z,	π^*2p_x,	π^*2p_y
Bonding MO's	$\sigma\, 2s$,	$\sigma\, 2p_z$,	$\pi\, 2p_x$,	$\pi\, 2p_y$

i. The increasing order of energies of various MO's for atoms with atomic number (Z) ≤ 7 e.g. H_2, C_2, N_2.

OR

For species with total number of electrons ≤ 14, e.g. CN^-, HF.

$\sigma\, 1s < \sigma^*\, 1s < \sigma\, 2s < \sigma^*\, 2s < (\pi\, 2p_x \equiv \pi 2p_y) < \sigma\, 2p_z < (\pi^*\, 2p_x \equiv \pi^*\, 2p_y) < \sigma^*\, 2p_z$.

ii. The increasing order of energies of various MO's for atoms with atomic number (Z) > 7 e.g. O_2 F_2.

OR

For species with total number of electrons > 14, e.g. NO.

$\sigma\, 1s < \sigma^*\, 1s < \sigma\, 2s < \sigma^*\, 2s < \sigma\, 2p_z < (\pi 2p_x \equiv \pi 2p_y) < \pi^*\, 2p_x \equiv \pi^*\, 2p_y > < \sigma^* 2p_z$.

iii. **Bond order:** It is one-half the difference between the number of electrons present in the bonding and the antibonding orbital, i.e.

$$\text{Bond order (BO)} = \frac{1}{2}(N_b - N_a)$$

Bond order may be fractional.

Integral and even zero.

$$\text{BO} \propto \Delta_{BE}H$$

and

$$\text{BO} \propto \frac{1}{\text{Bond length}}$$

iv. **Magnetic nature:** If all the MO's in a molecule are paired, the substance is diamagnetic. However, if one or more MO's are unpaired, it is paramagnetic e.g. O_2 molecule.

The magnetic moment (μ_{MM}) is calculated as

$\mu_{MM} = \sqrt{n\,(n+2)}$ BM (Bohr magneton)

where n is the number of unpaired electrons.

d. Bonding and their characteristics in some homonuclear diatomic molecules/ions are explained in Section 2.24.10.

e. Bonding and their characteristics in some heteronuclear diatomic molecules/ions are explained in Section 2.24.13.

15. Points to remember:

a. More is the number of bonds between two atoms, the shorter is the bond length.

b. $FeCl_2$ is less covalent than $FeCl_3$ because polarising power of Fe^{2+} is less than that of Fe^{3+} ion having smaller size and high oxidation state.

c. The solubility of aluminium halides decreases from AlF_3 to AlI_3 due to increase in the covalent character in accordance with Fajan's rule.

d. The dipole moment helps to predict whether a molecule is polar or non-polar.

e. A molecule may contain polar covalent bonds but its dipole moment may be zero if it is a symmetrical molecule.

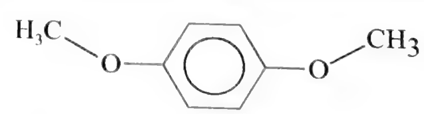
f. The dipole moment helps to predict geometry of molecules.

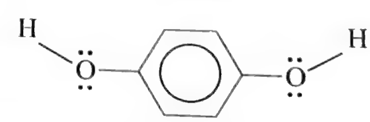
g. Dipole moment values can be used to distinguish between the *cis* and *trans* isomers, usually *cis* isomers have higher dipole moment and are more polar than the *trans* isomers.

h. The dipole moment of CO molecule is greater than expected due to the presence of coordinate bond.

i. Among the ortho-, meta- and para-isomers, dipole moment is the greatest for ortho-isomer and zero for para-isomer (same substituents). In general, dipole moment of $o > m > p$.

j. The dipole moments of p-dimethoxy benzene and 1, 4-dihydroxy benzene (i.e. quinol) are not zero ($\mu \neq O$), because of their structures shown as:





k. The maximum covalency is equal to the number of electrons present in the s and p-orbitals of the valence shell in the ground state.

l. The maximum number of covalent bonds formed between two atoms is never greater than three.

m. H-atom always forms only one σ-bond in the covalent compound.

n. A 'π-bond' is never formed alone. It is formed along with a 'σ' bond.

o. The ability of the hybrid orbitals to overlap is in the order: $sp^3 > sp^2 > sp$, i.e. greater is the p-character, greater is the ability to overlap

p. Decreasing order of the energy of orbitals:

$p > sp^3 > sp^2 > sp > s$ [Greater is the p-character, greater is the energy of orbitals.]

q. Decreasing order of bond angle of orbitals:

sp (180°) > sp^2 (120°) > sp^3 (109.5°) [Greater is the % of s-character greater is the bond angle.]

r. Decreasing order of the strengths of bonds formed by overlap of atomic orbitals:

$s - s > s - p > p - p$ [More is the overlap, more is the strength of bond formed.]

s. SF_4 has a see-saw structure.

t. Valence bond theory fails to explain the paramagnetic behaviour of substances and geometry of non-linear molecules.

u. Though bond order of $H_2^{\oplus}$ and $H_2^{\ominus}$ is same (i.e. ½), $H_2^{\ominus}$ is slightly less stable than $H_2^{\oplus}$ because $H_2^{\ominus}$ has one electron in the antibonding orbital resulting in repulsion (decrease instability).

v. Order of stability and bond dissociation energies are $O_2^{\oplus} > O_2 > O_2^{\ominus} > O_2^{2-}$ and $N_2 > N_2^{\oplus} = N_2^{\ominus} > N_2^{2-}$

w. The polarisability of the noble gases such as He, Ne, Ar, Kr and Xe increases in the order He < Ne < Ar < Kr < Xe. Xenon is the most polarisble because the molecular mass also increases in the same order.

2.1 INTRODUCTION

'The electrons serve as the bonds of union between atoms'. In this chapter, we seek the answers to some of the basic questions such as:

1. Why do atoms of the same elements or different elements combine to form compound? For example, hydrogen exists as H_2 and not as H_3.
2. Why do some atoms combine while certain others do not, e.g. two H-atoms combine to form H_2 but He-atoms do not combine to form He_2?
3. What are the forces which hold atoms together in molecules in different arrangements?
4. Why particular shapes are adopted by molecules e.g. CO_2 is linear but H_2O is a bent (V-shaped) molecule? Similarly, BCl_3 is planar but NH_3 is pyramidal.
5. What particular arrangement of ions in ionic compounds are preferred?

   The answers to the above questions have been given by different theories/concepts from time to time. These are as follows:

   a. Kössel–Lewis approach.
   b. Octet rule
   c. Formal charge
   d. Bond angle and bond order
   e. Different types of chemical bond, e.g. ionic, covalent and coordinate
   f. Dipole moment
   g. Valence bond theory (VBT)
   h. Valence shell electron pair repulsion (VSEPR) theory
   i. Molecular orbital theory
   j. Hybridisation
   k. Resonance
   l. Hydrogen bonding

2.2 MOLECULES

A group of atoms existing together as one species having characteristic properties is called a molecule e.g., O_2, H_2, N_2, H_2O, P_4, S_8

Chemical bond: The attractive force which holds various constituents (atoms, ions etc.) together in different chemical species is called a chemical force or a valence force. The association between atoms in a molecule is by valence forces is called a chemical bond.

2.3 OCTET RULE

Kössel and Lewis in 1916 developed an important theory of chemical combination between atoms known as *electronic theory of chemical bonding*. According to this, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shell. This is known as *octet rule*.

2.4 MODES OF CHEMICAL COMBINATION

The arrangement of electrons in noble gases is the criteria of stability, i.e. fully filled sub-shell (ns^2np^6). The atoms of these elements are in a state of great stability and hence do not form compounds and in general are chemically inert.

So, it is the valence electrons that determine the chemical behaviour of an atom. In a compound, a definite number of valence electrons are involved in the bonding process. The chemical association among atoms can be achieved by many ways depending upon the number of valence electrons contained in the atoms. Three major types of chemical bonding are as follows:

1. Ionic bonding: Stability through transfer of electrons.
2. Covalent bonding: Stability through mutual sharing of electrons.
3. Coordinate bonding: Stability through partial transfer and partial sharing of electrons.

2.5 KÖSSEL–LEWIS APPROACH TO CHEMICAL BONDING

Various attempts were made to explain the formation of chemical bonds in terms of electrons but it was only in 1916 when Kössel and Lewis succeeded independently in giving a satisfactory explanation. They were the first to give logical explanation of valence which was based on the inertness of noble gases.

Lewis pictured the atom in terms of (i) a positively charged 'Kernel' (the nucleus plus the inner electrons) and (ii) the outer shell that could accommodate a maximum of eight electrons. He further assumed that these eight electrons occupy the corners of a cube which surround the 'Kernel'.

Thus the single outer shell of Na (sodium) would occupy one corner of the cube, while in the case of a noble gas all the eight corners would be occupied. Thus, octet of electrons is said to have stable *electronic arrangement*.

Lewis postulated that atoms achieve the stable state octet when they are linked by chemical bonds. For example,

1. Na and Cl achieve stable state octet by transfer of an electron from Na to Cl, there by giving $Na^{\ominus}$ and $Cl^{\oplus}$ ions.
2. In case of other molecules such as Cl_2, H_2 and F_2 etc., the bond is formed by sharing a pair of electrons between the atoms. In this process, each atom attains a *stable outer octet of electrons*.

2.5.1 Lewis Symbols

In the formation of a molecule, only the outer shell electrons take part in chemical combination and they are known as *valence electrons*. The inner shell electrons are well protected and are generally not involved in the combination process. G.N. Lewis, an American chemist introduced simple notations to represent

valence electrons in an atom. These notations are called *Lewis symbols*. For example, the Lewis symbols for the elements of the second period are as under:

Li	Be	·B·	·C·	·N·	:O:	:F:	:Ne:

2.5.2 SIGNIFICANCE OF LEWIS SYMBOLS

The number of dots around the symbol represents the number of valence electrons. This number of valence electron helps to calculate the common of **group valence** of the element (Table 2.1). The group valence of the elements is generally either equal to the number of dots in Lewis symbols (if these are ≤ 4) or 8 minus the number of dots or the valence electrons (if these are >4).

Table 2.1 The valencies of the elements of the 2nd period:

Elements of the 2nd period	Li	Be	B	C	N	O	F	Ne
Valency	1	2	3	4	3	2	1	0
	Equal to the no. of dots.				Equal to 8 minus the no. of dots.			

2.5.3 VARIABLE COVALENCY

The elements of the 2nd period as shown in Table 2.1 does not have *d*-orbitals in their valence shell. However, the elements having vacant *d*-orbitals in their valence shell such as P, S, Cl, Br and I show *variable covalency* by increasing the number of unpaired electrons under the excited conditions, i.e. unpairing the paired and shifting the electrons to vacant *d*-orbitals.

Such a shifting is not possible in case of elements of the 1st and 2nd periods (e.g. H, Be, N, O and F) because of the absence of d-orbitals in their valence shell.

Some examples of variable covalency are as follows:

1. Phosphorous (P) shows 3 and 5 covalencies.
2. Sulphur atom (S) shows 2, 4 and 6 covalencies:
3. Chlorine shows variable valency of 1, 3, 5, 7.

Thus variable covalency is shown by those elements which have vacant, *d*-orbitals in their valence shell.

4. Fe forms Fe^{2+} and Fe^{3+} ions: Fe (Z = 26), $3d^6\,4s^2$

   $Fe^{2+} = 3d^6$ (unstable core)

   $Fe^{3+} = 3d^5$ (stable half-filled *d*-orbitals)

   The most stable ion forms stable configuration after the loss of valence electrons.

   Thus, Fe^{3+} salts are more stable than Fe^{2+} salts.

5. Cu forms $Cu^{\oplus}$ and Cu^{2+} ions and Cu^{2+} salts are more stable than Cu^{+1} ions. Cu (Z = 29), $3d^{10}\,4s^1$

   $Cu^{\oplus} = 3d^{10}$ (stable configuration)

   $Cu^{2+} = 3d^9$ (more stable configuration)

   The greater stability of Cu^{2+} than $Cu^{\oplus}$ ion is due to the fact that the nuclear charge of Cu is not sufficient enough to hold 18 e^-'s of $Cu^{\oplus}$ ion present in the outermost shell.

6. Similarly, the lower oxidation state of heavier *p*-block elements is more than higher oxidation state, due to inert pair effect as explained in Chapter 1.

   Examples:

   $Tl^{\oplus}$ is more stable than Tl^{3+}.

   Sn^{2+} and Pb^{2+} are more stable than Sn^{4+} and Pb^{4+}.

   Sb^{3+} and Bi^{3+} are more stable than Sb^{5+} and Bi^{5+}.

2.6 IONIC OR ELECTROVALENT BOND

The following is a list of Kössel's postulation:

1. In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases.
2. The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms.
3. The negative and positive ions thus formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has a duplet of electrons) have a particularly stable outer shell configuration of eight (octet) electrons, ns^2np^6.
4. The negative and positive ions are stabilised by electrostatic attraction.

   Examples:

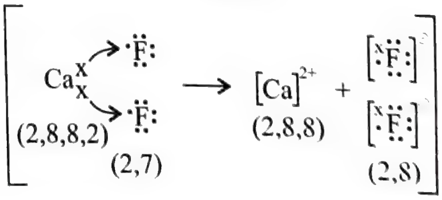
   a. Similarly, the formation of CaF_2 may be shown as:

   $$\underset{[Ar]\,4s^2}{Ca^{xx}} \longrightarrow \underset{[Ar]}{Ca^{2+} + 2e^-}$$

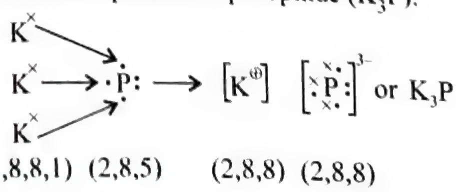
   $$\underset{[He]\,2s^2\,2p^5}{:\ddot{F}: + e^{\ominus}} \longrightarrow \underset{[He]\,2s^2\,2p^6 \text{ or } [Ne]}{F^{\ominus}}$$

   $$Ca^{2+} + 2F^{\ominus} \longrightarrow CaF_2 \text{ or } Ca^{2+}(F^{\ominus})_2$$

   OR

   b. Formation of potassium phosphide (K_3P):

The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as the electrovalent bond. The electrovalence is thus equal to the number of unit charge(s) on the ion.

Thus, calcium is assigned a positive electrovalence of two, while chlorine a negative electrovalence of one.

Kössel's postulations provide the basis for the modern concepts regarding ion-formation by transfer and the formation of ionic crystalline compounds. His views have proved to be of great value in the understanding and systematisation of the ionic compounds. At the same time, he did recognise the fact that a large number of compounds did not fit into these concepts.

2.6.1 Favourable Conditions for the Formation of Ionic Bonds

1. Low ionisation energy (IE) of the atom forming the cation easily.
2. High electron gain enthalpy ($\Delta_{eg}H^{\ominus}$) or electron affinity (EA) of the atom forming the anion easily.
3. High negative lattice enthalpy ($\Delta_U H^{\ominus}$) of the crystal formed.

Note: i. Lattice enthalpy $\propto$ magnitude of charge of cation and anion.

ii. $\Delta_U H^{\ominus} \propto$ small cation and $\propto$ large anion.

Examples:

a. The lattice energy of $Mg^{2+}\ Cl_2^{-1\times2}$ is greater than that of $Na^{\oplus}Cl^{\ominus}$ (due to high charge in $MgCl_2$).

b. The lattice energy of NaCl is greater than that of CsCl, as $Na^{\oplus}$ cation is smaller than $Cs^{\oplus}$ cation, though the IE of Cs is much lower than that of Na.

The smaller is the cation, the more effective is the nucleus in attracting the neighbouring anions towards it, and thus the lattice formed is highly stable and hence compounds have high (negative) lattice energy.

4. If total ionisation enthalpy (IE) + Total electron gain enthalpy ($\Delta_{eg}H^{\ominus}$) – Total lattice enthalpy ($\Delta_U H^{\ominus}$) < 0.

OR

If lattice enthalpy ($\Delta_U H^{\ominus}$) + Electron affinity (EA) or electron gain enthalpy ($\Delta_{eg}H^{\ominus}$) > Ionisation enthalpy (IE)

The net effect will be the release of energy and hence an ionic bond is formed.

Note: Sometimes $\Delta_{eg}H^{\ominus}$ is used in place of EA (refer to Chapter 1). EA and $\Delta_{eg}H^{\ominus}$ are taken as equal in magnitude (as $\Delta_{eg}H^{\ominus}$ is only slightly higher than EA) but opposite in sign. $\Delta_{eg}H^{\ominus}$ has same sign as required according to thermodynamics, i.e. if energy is released, it is given a –ve sign and vice versa. EA has sign contrary to thermodynamics convention.

5. Most of the ionic compounds are formed between metal cations (due to low IE) and non-metal anions (due to high (negative) EA), except $NH_4^{\oplus}$ ion, i.e. a cation formed from two non-metallic elements (N and H). A large number of ionic compounds are known in while $NH_4^{\oplus}$ is the cation.
6. For the formation of ionic bond between two atoms, the EN difference between them should be ≥1.9.
7. **Method of writing formulas of an ionic compound:**

a. Write the symbols of the ions side of side in such a way that +ve ion on the left and –ve ion on the right as XY (Let X is cation and Y is anion).

b. Write their electrovalencies in figure on the top of each symbol as $X^a\ Y^b$. (Let a and b are valencies of cation and anion respectively.)

c. Divide their valencies by HCF.

d. Apply criss-cross rule as $\overset{a}{X} \times \overset{b}{Y}$ i.e. formula of $X_b\ Y_a$. (Consider only magnitude of valencies.)

e. Check total +ve and –ve charges in the compound should be equal.

Examples:

1. Calcium phosphate $\Rightarrow \overset{2+}{Ca} \times \overset{3-}{(PO_4)} \equiv \overset{+2\times3}{Ca_3}\ \overset{-3\times2}{(PO_4)_2}$
2. Zirconium phosphate $\Rightarrow \overset{4+}{Zr} \times \overset{3-}{(PO_4)} \equiv \overset{+4\times3}{Zr_3}\ \overset{-3\times4}{(PO_4)_4}$

2.6.2 Characteristics of Ionic Compounds

The following are some of the general properties shown by these compounds:

1. **Crystalline nature:** These compounds are usually crystalline in nature with constituent units as ions. Force of attraction between the ions is **non-directional** and extends in all directions. Each ion is surrounded by a number of oppositely charged ions and this number is called **coordination number**. Hence, they form three-dimensional solid aggregates. Since electrostatic forces of attraction act in all directions, therefore, the ionic compounds do not possess directional characteristic and hence do not show stereoisomerism.
2. Due to the strong electrostatic attraction between these ions, the ionic compounds have high melting and boiling points.
3. In solid states the ions are strongly attracted and hence are not free to move. Therefore, in solid state, ionic compounds do not conduct electricity. However, in fused state or in aqueous solution, the ions are free to move and hence conduct electricity.
4. **Solubility:** Ionic compounds are fairly soluble in polar solvents and insoluble in non-polar solvents. This is because the polar solvents have high values of dielectric constant which is defined as the capacity of the solvent to weaken the force of attraction between the electrical charges immersed in that solvent. This is why water, having high value of dielectric constant, is one of the best solvents.

The solubility in polar solvents like water can also be explained by the dipole nature of water where the oxygen of water is the negative and hydrogen being positive, water molecules pull the ions of the ionic compound from the crystal lattice. These ions are surrounded by water dipoles with the oppositely charged ends directed towards them.

These solvated ions lead an independent existence and are thus dissolved in water. The electrovalent compound dissolves in the solvent if the value of the solvation energy is higher than the lattice energy of that compound.

$$AB + \text{Lattice energy} \longrightarrow A^{\oplus} + B^{\ominus}$$

These ions are surrounded by solvent molecules. This process is exothermic and is called solvation.

$$A^{\oplus} + x\,(\text{solv.}) \longrightarrow [A\,(\text{solv.})_x]^{\oplus} + \text{energy}$$

$$B^{\ominus} + y\,(\text{solv.}) \longrightarrow [B\,(\text{solv.})_y]^{\ominus} + \text{energy}$$

The value of solvation energy depend on the relative size of the ions. The smaller the ions more the solvation. The non-polar solvents do not solvate ions and thus do not release energy due to which they do not dissolve ionic compounds.

Note: The dielectric constant of H_2O (82) is slightly more than that of D_2O (80.5). The dielectric constant of a solvent is defined as its capacity to weaken the force of attraction between the electrical charges immersed in that solvent.

5. **Ionic reactions:** Ionic compounds furnish ions in solutions. Chemical reactions are due to the presence of these ions.
6. **Space isomerism:** The electrovalent bond is non-rigid and non-directional and therefore these compounds do not show space or stereoisomerism.
7. **Isomorphism:** Ionic compounds show isomorphism properties. Compounds having similar chemical constitution (i.e. having same formula) and having same electronic configuration are isomorphous to each other.

   For example,

i. K_2SO_4 and K_2CrO_4 ii. $ZnSO_4{\cdot}7H_2O$ and $MgSO_4{\cdot}7H_2O$	Isomorphous due to same formula
iii. $\underset{(2,8)}{\overset{1+}{Na}}\ \underset{(2,8)}{\overset{1-}{F}}$ and $\underset{(2,8)}{\overset{2+}{Mg}}\ \underset{(2,8)}{\overset{2-}{O}}$	Isomorphous due to same electronic configuration
iv. $\underset{(2,8,8)}{2K^{\oplus}}\ \underset{(2,8,8)}{S^{2-}}\,(K_2S)$ and $\underset{(2,8,8)}{K^{\oplus}}\ \underset{(2,8,8)}{Cl^{\ominus}}\,(KCl)$ and $\underset{(2,8,8)}{Ca^{2+}}\ \underset{(2,8,8)}{2Cl^{\ominus}}\,(CaCl_2)$	

ILLUSTRATION 2.1

1. Which statement is correct for ionic bond?
   a. It is non-directional.
   b. It is formed by overlapping of orbitals.
   c. It is formed by the elements with same EN.
   d. Both (a) and (b) are correct.
2. Which one is having high hydration energy?
   a. $K^{\oplus}$ b. $Li^{\oplus}$ c. $Na^{\oplus}$ d. $Cs^{\oplus}$
3. Which statement is/are correct (more than one correct)?
   a. In aqueous solution Al gives hydrated ions $[Al(H_2O)_6]^{3+}$.
   b. Most of aluminium compounds are covalent because formation of Al^{3+} requires much more energy (= 5138 kJ mol^{-1}) which is not available ordinarily.
   c. In aqueous solution Al forms hydrated ions because of high (negative) heat of hydration of Al^{3+} compensates the high IE_3 of Al.
   d. Magnitude of hydration energy of $Al^{3+} < IE_3$ of Al.
4. Which statement is/are correct?
   a. Formation of anions with unit charge (e.g. $Cl^{\ominus}$, $Br^{\ominus}$, $I^{\ominus}$) are very common because the EA's of these atoms is positive and quite high or $\Delta_{eg}H^{\ominus}$ of these atoms are negative and quite high.
   b. EA's of above atoms (Cl, Br, I) is negative, and quite high or $\Delta_{eg}H^{\ominus}$ of these atoms is positive and quite high.
   c. Formation of anions with –2 charge (e.g. S^{2-}, O^{2-}) is not so easy as their second EA's are negative, i.e. energy is needed to add second electron.
   d. Formation of anions with –3 charge (e.g. N^{3-}, P^{3-}) is almost rare as the third $\Delta_{eg}H^{\ominus}$ are positive, i.e., energy in needed to add third electron.
5. Which statement is/are correct?
   a. Ionic compounds like sulphate and phosphates of Ba and Sr [e.g. $BaSO_4$, $SrSO_4$, $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$] are insoluble in water.
   b. The above compounds are soluble in water.
   c. Magnitude of lattice energy ($\Delta_U H^{\ominus}$) of the above compounds is greater than their hydration energy ($\Delta_{hyd}H^{\ominus}$). High $\Delta_U H^{\ominus}$ of these compounds is due to polyvalent nature of both the cations and the anions.
   d. In these cases, hydration of ions fails to liberate sufficient energy to offset the lattice energy.

Sol. **1. a.** **2. b.** **3. a, b, c** **4. a, c, d** **5. a, c, d.**

1. a. Factual statement.
2. b. Higher the charge density $\left(\dfrac{\text{charge}}{\text{size}}\text{ ratio}\right)$, higher is the hydration energy.
3. a, b and c are correct statements.
4. a, c, d.

   Note: By convention EA is assigned as +ve but $\Delta_{eg}H^{\ominus}$ is assigned as –ve value for exothermic processes (i.e., energy is released) and vice versa. So statements *a*, *c* and *d* are correct.
5. a, c, d: If hydration energy ($\Delta_{hyd}H^{\ominus}$) > lattice energy ($\Delta_U H^{\ominus}$). The compound is soluble in water. So, statements a, c and d are correct.

2.7 COVALENT BOND: LANGMUIR AND LEWIS CONCEPT

Langmuir (1919) refined the Lewis postulations by rejecting the idea of the stationary cubical arrangement of the octet and by introducing the term *covalent bond.*

The Lewis–Langmuir theory suggests that when both the atoms taking part in a chemical combination are short of electrons than the nearest noble gas configuration, they can share the electrons in order to complete their octets. Each atom contributes the same number of electrons to form common pairs which are then shared by both atoms.

Certain elements which have high ionisation energies are incapable of transferring and other having low electron affinities, fail to take up electrons. The atoms of such elements share their electrons with the atoms of other elements (and sometimes among themselves) in such a manner that both the atoms form complete outer shell. In this manner, they achieve stability. Such an association through sharing of electron pairs among of different or of same kinds is known as covalent bond. This was proposed by G.N. Lewis.

The covalent bonding can be achieved in two ways:

1. Sharing of electrons between atoms of same kinds, e.g. formation of Cl_2, F_2, O_2, N_2 etc.
2. Sharing of electrons between atoms of different kinds, e.g. formation of H_2O, HCl, NH_3, CO_2, CH_4, etc.

Examples:

Formation of chlorine molecule, Cl_2: Each Cl atom with electronic configuration, [Ne]$3s^2$, $3p^5$, is one electron short of argon (Ar) configuration. Each Cl atom contributes one electron to form a common shared pairs. In this process, both chlorine atoms attain the outer shell octet of the nearest noble gas (i.e. argon) (Fig. 2.1).

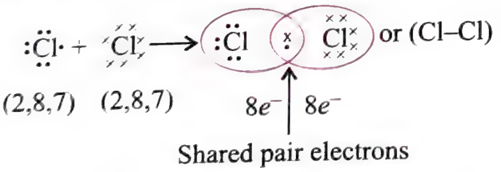


Fig. 2.1 Covalent bond between two Cl atoms

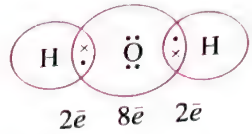
In the examples above, each atom contributes one electron. Hence, the covalency of Cl and H is 1. The bond formed is called *single covalent-bond* and is represented by single line (—) between the two atoms.

2.7.1 REPRESENTATION OF LEWIS SYMBOLS

The dots or (x) represent electrons. Such structures are referred to as Lewis dot structures.

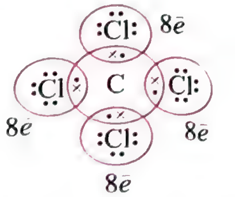
The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different. *The important conditions being that:*

1. Each bond is formed as a result of sharing of an electron pair between the atoms.
2. Each combining atom contributes at least one electron to the shared pair.
3. The combining atoms attain the outershell noble gas configurations as a result of the sharing of electrons.
4. Thus in water and carbon tetrachloride molecules, formation of covalent bonds can be represented as shown in Figs. 2.2(a) and 2.2(b).



H atoms attain a duplet of electrons and O, the octet

(a)



Each of the four Cl atoms along with the C atoms attain octet of electron

(b)

Fig. 2.2 (a) and (b) Covalent bond in H_2O and CCl_4

2.7.2 MULTIPLE COVALENT BOND

When two atoms share one electron pair they are said to be joined by a single covalent bond. In many compounds, the multiple bonds between atoms are formed.

Multiple bonds may also be formed by the sharing of two or three electrons by each of two atoms. The bond thus formed is called *double* or *triple bond* and are represented by a double line (=) and a triple line (≡) respectively.

Examples:

1. Formation of CO_2 and C_2H_4 (ethene) moleucle, containing double (=) bonds.

   In the CO_2 molecule, two double bonds are formed by sharing two electrons of each C and O atoms. Similarly, in ethene (C_2H_4 or $H_2C=CH_2$) molecule the two C-atoms are joined by a double bond. (Figs. 2.3(a) and 2.3(b).

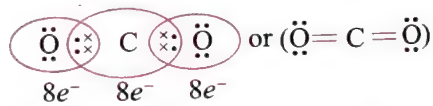


Fig. 2.3 (a) Double bonds in CO_2 molecule.

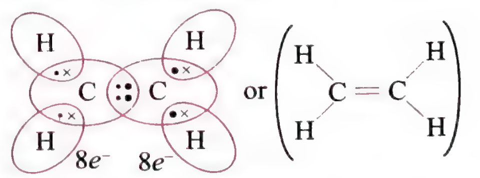


Fig. 2.3 (b) Double bonds in ethene (C_2H_4 or $H_2C=CH_2$) molecule.

2. Formation of N_2 and C_2H_2 (ethyne) molecule containing triple (≡) bonds.

   In the N_2 molecule one triple bond is formed by sharing three electrons of each N atoms. Similarly in ethyne (C_2H_2 or HC ≡ CH) molecule, two C-atoms are joined by a triple bond (Figs. 2.4(a) and 2.4(b)).

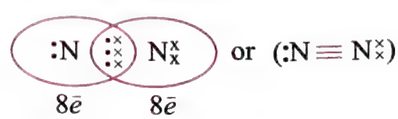
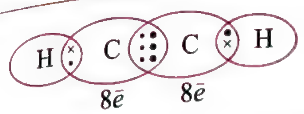


Fig. 2.4 (a) Triple bond in N_2 molecule



or (H—C≡C—H)

Fig. 2.4 (b) Triple bond in ethyne (C_2H_2 or HC ≡ CH) molecule

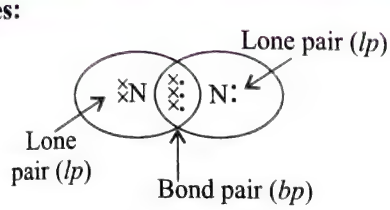
2.7.3 Lone Pairs and Bond Pairs

The valence electrons not involved in bonding (i.e. sharing) are shown as such and depicted as (•• or ××) are called *lone pairs (lp)* or *non-bonding electrons* or *unshared pairs*.

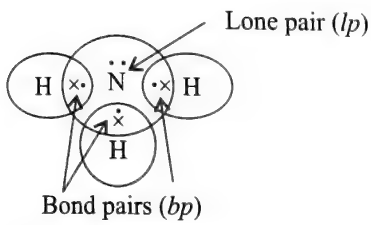
The shared pairs of electrons present between the atoms are called *bond pairs (bp)* because they are responsible for the formation of bonds between the atoms.

Note: Sometimes they are depicted as (x .), in which (x) represents an electron from one type of atom and (.) also represents an electron from another same or different type of atom, for clear understanding of shared pair electrons.

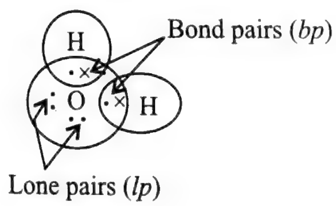
Examples:

1. 

(N_2 molecule)

2. 

(NH_3 molecule)

3. 

(H_2O molecule)

2.7.4 Characteristics of Covalent Compounds

1. **Physical state:** Generally these compounds exist as liquid or gases of low boiling point, under the normal conditions of temperature and pressure. Some compounds having high molecular masses exist as soft solids, e.g. S_8, P_4 and I_2 are soft solids.

   This is due to the presence of weak forces of attraction (van der Waals forces) between the molecules.

2. **Melting and boiling points:** They have relatively low melting and boiling points, due to the presence of weak attractive forces between them. Exceptions are diamond, SiC (carborundum), SiO_2 (silica), which have giant three-dimensional structures.

3. **Crystal structures:** These are of three types:
   a. The crystals in which the unit is molecule and are held by van der Waals forces, readily fusible and volatile, e.g. S_8, I_2 and P_2O_5 etc.
   b. The crystals having separate lattice layers, e.g. graphite. Each atom has 3 neighbours and 2 atoms of them are bonded by a single covalent bond and to the 3rd atom by double bond. These layers are bonded by tightly together into a layer. These layers can slide on one another which accounts for the softness of graphite.
   c. The crystals in which every atom is bonded to 4 other, atoms by single covalent bonds to form giant structures. These are very hard with high melting points. e.g. SiC and AlN.

4. **Solubility:** Generally, they are insoluble in polar solvents (e.g. water) but soluble in non-polar solvents (e.g. benzene, CCl_4, ether, etc.), due to the principle 'like dissolves like'.

   Exceptions are alcohols and amines which dissolve in water due to hydrogen bonding.

   Covalent solids having three-dimensional giant structures are practically insoluble in all solvents.

5. **Electrical conductivity:** Generally, they are bad conductors of electricity. Some polar compounds such as HCl in solution conducts electricity.

   The graphite conducts electricity because electron can pass from one layer to the other. But covalent solids having three-dimensional giant structures are bad conductors because they do not contain charged particles or free electrons.

6. **Isomerisation:** The covalent bond is directional and rigid. Thus, there is a possibility of different arrangements of atoms in space. Thus, they can show structural and space isomerism.

7. **Molecular reactions:** They show molecular reactions but reaction rates are usually low because these reactions involve two steps.
   a. Breaking of covalent bonds of the reactants.
   b. Formation of new bonds while the ionic reactions involve only regrouping of ions.

2.7.5 Comparison Between Ionic and Covalent Compounds

	Ionic compound	Covalent compound
1.	Crystalline solids at room temperature.	Gases, liquids or soft solids under ordinary conditions.
2.	Hard and brittle.	Soft and waxy with the exception of giant molecules.
3.	High melting and boiling points.	Low melting and boiling points with the exception of giant molecules.

4.	In solid state, bad conductors of electricity. Good conductors in molten state and in solutions.	Bad conductors of electricity with few exceptions having layer lattice structure.
5.	Freely soluble in water and in polar solvents. Insoluble in non-polar solvents.	Usually insoluble in water and in polar solvents. Soluble in non-polar solvents.
6.	Undergoes ionic reactions. Rates of reactions are very high. Reactions are fast and instantaneous.	Undergoes molecular reactions. Rates of reactions are low. Reactions are slow.

2.7.6 Comparison Between Ionic and Covalent Bonds

	Ionic bond	Covalent bond
1.	Formed by the transference of electron or electrons from electropositive (metal) to electronegative (non-metal) atoms. Such a bond is possible between dissimilar atoms.	Formed by sharing of electrons between two non-metal atoms when the electrons are equally contributed by both the atoms. Such a bond is possible between similar and dissimilar atoms.
2.	Non-rigid and non-directional, does not cause isomerism.	Rigid and directional, causes space and structural isomerism.
3.	Consists of electrostatic force between atoms.	Consists of shared pair or pairs of electrons which are attracted by both the nuclei.
4.	It is polar in nature.	It is non-polar if the electronegativity difference is zero or small.
5.	It is a weak bond, because the electrostatic force between the ions can be broken easily.	It is a strong bond, because the paired electrons cannot be separated easily.

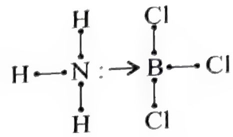
2.7.7 Limitations of Lewis–Langmuir Concept of Covalent Bond

1. It could not explain the shapes of the molecules containing covalent bonds.
2. It could not explain how the molecules such as H_2, Cl_2 and Br_2 etc. in which there are no ions and hence there are no electrostatic forces of attraction of a covalent bond.
3. It could not explain the release of energy during the formation of a covalent bond.

2.8 Coordinate (or) Dative (or) Semipolar (or) Co-ionic (or) Donor Acceptor Bond

Perkins (1921) postulated a related type of bond formation in which the electron pair used for sharing is donated solely by one of the combining atoms. For example, in the combining of ammonia, NH_3, with boron trichloride, BCl_3, the avaliable electron pair on the nitrogen atom in ammonia is donated to boron of BCl_3 which accepts it resulting in the formation of a bond between NH_3 and BCl_3. The structure satisfies the octet rule for B, N and Cl atoms.

Alternatively: The process of donation of the electron pair by one atom and its acceptance by the other atom is represented as electronic charge displacement, resulting in the formation of a dipolar molecule.



The arrow (→) shown in the structure indicates donor–acceptor relationship. Thus the nitrogen atom in NH_3BCl_3 would acquire a formal positive charge and the boron atom a formal negative charge, $H_3\overset{\oplus}{N}\overset{\ominus}{B}Cl_3$

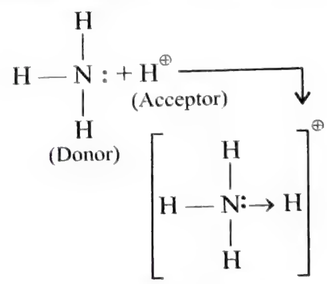
This type of bond has been variously named as semi-polar, coordinate, dative, co-ionic or donor–acceptor bond.

The atom or ion or molecule with one unshared electron pair (or lone pair or *lp*) which it can donate is called a *Lewis base* or ligands whereas those which accepts the lone pair are called *Lewis acids*. In the above example, NH_3 is a Lewis base while BCl_3 is a Lewis acid.

Note: $H^{\oplus}$ ions and cations of transition metals such as Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} etc. acts as Lewis acids.

2.8.1 Some More Examples of Coordinate Bond

1. **Formation of $\overset{\oplus}{NH_4}$ ion:** $H^{\oplus}$ion has no electrons and thus accepts a lone pair (*lp*) from N-atom of NH_3 molecule.



2. **Formation of O_3:** O_2 molecule consists of two O-atoms linked by a double covalent bonds. Each O-atom has two *lp*'s of e^-'s. One *lp* of electrons is donated to the third O-atoms, which has 6 e^-'s, a coordinate bond is formed.

(Donor or Lewis base) (Acceptor or Lewis acid)

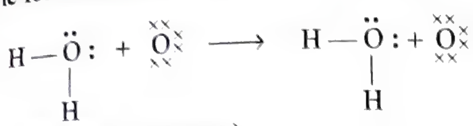
3. **Formation of CO:** C-atom has four valence electrons and O-atom has six valence electrons and they combine to form

a bond and a coordinate bond from O to C, to complete their octet.

Acceptor Donor

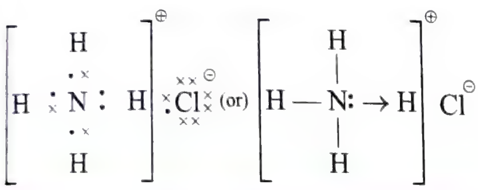
Note: The dipole moment of CO molecule is greater than expected due to the presence of coordinated bond.

4. **Formation of H_2O_2:** O-atom in H_2O has two *lp*'s of electrons and one *lp* is donated to another O-atom resulting in the formation of coordinate bond in H_2O_2.



(Donor) (Acceptor)

5. **Compounds having electrovalent, covalent and coordinate bonds, e.g. [NH_4Cl]:** There is ionic bond between $NH_4^{\oplus}$ and $Cl^{\ominus}$ ions. In $NH_4^{\oplus}$ ion, there are three covalent and one coordinate bonds as shown.



Note: In the modern terminology, there is no distinction between a covalent and a coordinate bond. The bond formed is indistinguishable from a normal covalent bond because all electrons are similar irrespective of their source. The distinction, however, is useful of the extent that it helps in keeping track of valence electrons and for assigning formal charges.

2.8.2 Characteristics of Coordinate Compounds

The properties of coordinate compounds are intermediate between the properties of electrovalent compounds and covalent compounds. The main properties of coordinate compounds are given below:

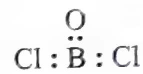
1. **Physical state:** These exist as gases, liquids and solids under ordinary conditions.
2. **Melting and boiling points:** Their melting and boiling points are higher than purely covalent compounds and lower than purely ionic compounds.
3. **Stability:** These are as stable as the covalent compounds. The additional compounds are, however, not very stable. It is also a strong bond because the paired electrons cannot be separated easily.
4. **Solubility:** These are sparingly soluble in polar solvents such as water but readily soluble in non-polar (organic) solvents.
5. **Conductivity:** Like covalent compounds, these are also bad conductros of electricity. The solutions or fused masses do not allow the passage of electricity.
6. **Isomerism:** The bond is rigid and directional. Thus, coordinate compounds show isomerism.
7. **Dielectric constant:** Compounds containing coordinate bond have high values of dielectric constants.
8. **Molecular reactions:** These undergo molecular reactions. The reactions are slow.

2.9 LIMITATIONS OF THE OCTET RULE

The octet rule, though useful, is not universal. It is quite useful, for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

2.9.1 Incomplete Octet of the Central Atom

In some compounds, the number of electrons surrounding the central atom is less than eight, This is especially the case with elements having less than four valence electrons. Examples are as follows:

Li : Cl, H : Be : H, 

Li, Be and B have 1, 2 and 3 valence electrons only. Other such compounds are $AlCl_3$ and BF_3.

Such compounds are called *hypovalent* compound.

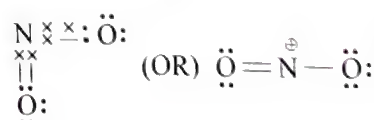
2.9.2 Odd Electron Molecules

In molecules with an odd number of electrons such as nitric oxide (NO) and nitrogen dioxide (NO_2), the octer rule is not satisfied for all the atoms.

Note: $3e^-$ bond is equivalent to half covalent bond.

Examples:

1. Superoxide ion ($O_2^{\ominus}$) 
2. Nitric oxide (NO) 
3. Nitrogen dioxide (NO_2)

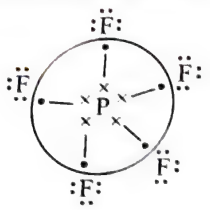


2.9.3 Expanded Octet

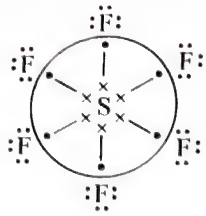
Elements in and beyond the third period of the periodic table have, apart from 3*s* and 3*p* orbitals, 3*d* orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the *expanded octet*. Obviously, the octer rule does not apply in such cases.

The elements which have more than $8e^-$'s is also called *hypervalent atom*.

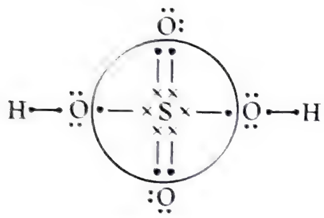
Some of the examples of such compounds are PF_5, SF_6, H_2SO_4 and IF_7 and a number of coordination compounds.



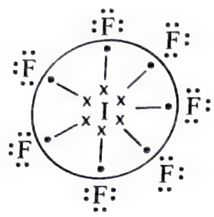
(PF_5)
(10 e^-'s around P atom)



(SF_6)
(12 e^-'s around S atom)



(H_2SO_4)
(12 e^-'s around S atom)



(IF_7)
(14 e^-'s around I atom)

[The elements P, S and F are hypervalent atoms and these compounds are called hypervalent compounds.]

Sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride the S atom has an octet of electrons around it.

:Cl—S—Cl: (or) :Cl : S : Cl:

Note: The formation of PF_5, SF_6 and IF_7 are explained in terms of hybridisation of *s*, *p* and *d*-orbitals such as sp^3d, sp^3d^2 and sp^3d^3 respectively.

2.9.4 Other Drawbacks of the Octet Theory

1. It does not account for the shape of molecules.
2. Octet rule is based upon the chemical inertness of noble gases. However, some noble gases (e.g., Xe (xenon) and Kr (Krypton) also combine with oxygen and fluorine to form a number of compounds such as XeF_2, XeF_4, $XeOF_4$, XeO_3, $XeOF_2$, XeO_2F_2, KrF_2, etc.
3. It does not explain the relative stability of the molecule and being totally silent about the energy of the molecule.

2.10 Lewis Representation of Simple Molecules (The Lewis Structures)

The Lewis dot structures provide a picture of bonding in molecule and ions in terms of the shared pairs of electrons and the octet rule.

Lewis structure has a number of limitations such as:

1. It does not explain the bonding and behaviour of a molecule completely.
2. It does not help in understanding the formation and properties of a molecule to a large extent.

Hence, writing of Lewis dot structures of molecules and ions is very useful.

2.10.1 Rules for Writing the Lewis Dot Structures

First method:

Step 1: Count the total number of valence electrons of the combining atoms. For example, in the CH_4 molecule there are eight valence e^-'s (4 from C and 4 from H atoms)

Step 2: For anions, add the number of electrons equal to the –ve charge. For cations, subtract the number of electrons equal to the +ve charge.

This gives the total number of electrons to be distributed.

Examples:

a. For the CO_3^{2-} ions, the two –ve charges indicate that two electrons have to be added to the total number of valence electrons.

(Total no. of electrons in CO_3^{2-}) = (Total no. of valence e^-'s of C-atom) + Total no. of valence e^-'s of three O-atoms $+2e^-$ (from two –ve charge)

$= 4 + [3\times 6] + 2 = 24\ e^-$'s

b. For $\overset{\oplus}{N}H_4$ ions, one +ve charge indicates the one electron has to be subtracted from the total number of valence electrons.

(Total no. of e^-'s in $\overset{\oplus}{N}H_4$) = Total no. of valence e^-'s of N atom + Total no. of valence e^-'s from four H-atoms – one e^- (from one +ve charge)

$= 5 + [4 \times 1] - 1 = 8\ e^-$'s

Step 3. In general, the least EN atoms occupies the central positon in the molecule/ion. For example, in NF_3 and CO_3^{2-}, N and C are the central atoms whereas the F and O atoms occupy the terminal position.

Therefore, select the central atom and draw the skeletal structure of the compound by intelligent guess to indicate which atom is linked to which other atom.

Step 4. Put one shared pair of electrons between every two atoms to represent a single bond between them. Use the remaining electron pairs either for multiple bonding or to show them as the lone pairs (*lp*'s). The basic requirement being that each bonded atom gets an octet of electrons.

Second method:

Sept 1: Calculate the total number of valence electrons after the addition of electrons for anions and/or substracting for the cations. Let it be V (symbol for valence e^-'s).

Step 2: Calculate the number of electrons for the complete octet of all the atoms. Let it be O (symbol for electrons for octet).

Step 3: Calculate the number of electrons as shared electrons (S) by subtracting V from O.

i.e., $S = O - V$

Step 4: Draw the skeletal structure and represent the shared pairs.

Step 5: Complete the structure by representing the unshared electrons (i.e., lone pairs) represented as U, i.e. (U = V – S).

For example, *Lewis structure of CO_2:*

Step 1. V = 1 × 4 (for C) + 2 × 6 (for O) = 16 e^-'s

Step 2. O = 1 × 8 (for C) + 2 × 8 (for oxygen) = 24 e^-'s

Step 3. S = O – V (24 – 16) = 8 e^-'s (shared)

Step 4. Draw the skeletal structure with shared pairs.

O :: C :: O (8 shared pair e^-'s)

Step 5. U = (V – S) = 16 – 8 = 8

(8 unshared or 4 lone pair e^-'s)

Lewis structure is as follows:

:Ö=C=Ö:

ILLUSTRATION 2.2

Write the Lewis dot structure of CO_3^{2-} ion.

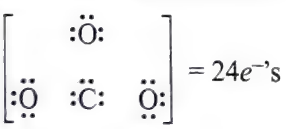
Sol. **Using the first method:**

Step 1: Total number of valence electrons in CO_3^{2-} ion = 4 + [3 × 6] + 2 = 24 e^-'s

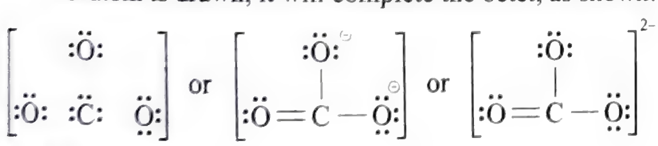
Step 2: The skeletal structure of CO_3 is

O
O C O

Step 3: Put one shared pair of electrons between each C and O and complete the octet of O-atom.



Step 4: In the above structure, octet of C is not complete. Therefore, multiple bonding is needed between C and O-atoms. If a double bond between C and one O-atom is drawn, it will complete the octet, as shown:



Second method:

Step 1: V (Total no. of e^-'s) = 1 × 4 (for C) + 3 × 6 (for O) + 2 (for 2(–ve) charge)

= 24 e^-'s.

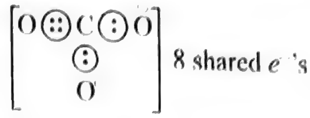
Step 2: O (Total no. of e^-'s for octet)

= 1 × 8 (for C) + 3 × 8 (for oxygen)

= 32 e^-'s

Step 3: S (Shared e^-'s) = (O – V) = (32 – 24) = 8 e^-'s.

Step 4: Skeletal structure with shared e^-'s.



Step 5: U (unshared e^-'s) = (V – S) = 24 – 8 = 16 e^-'s

Step 6: Add 16 unshared e^-'s to complete the Lewis structure.

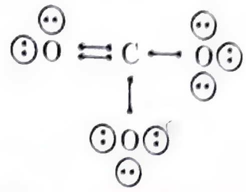


ILLUSTRATION 2.3

Write the Lewis structure for SO_5^{2-} (Per-oxodisulphate ion).

Sol. **Using the second method:**

Step 1: V (Total no. g e^-'s)

= 1 × 6 (for S) + 5 × 6 (for O) + 2 (for two –ve charge)

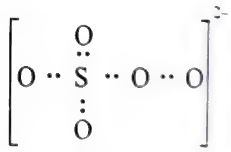
= 38 e^-'s

Step 2: O (Total no. of e^-'s for octet)

= 1 × 8 (for S) + 5 × 8 (for O) = 48 e^-'s

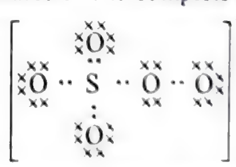
Step 3: S (Shared e^-'s) = (O – V) = 48 – 38 = 10 e^-'s

Step 4: Skeletal structure with 10 shared e^-'s



Step 5: U (unshared e^-'s) = (V – S) = 38 – 10 = 28 e^-'s

Step 6: Add 28 unshared e^-'s to complete the Lewis structure.



Note: (×) represents one unshared electrone. So, the number of unshared e^-'s = 28.

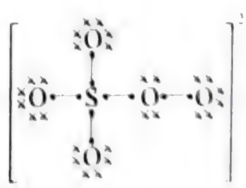
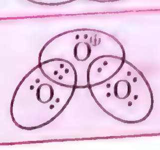
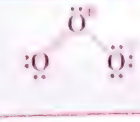
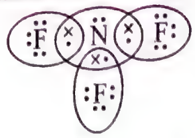
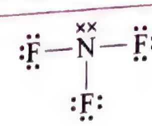
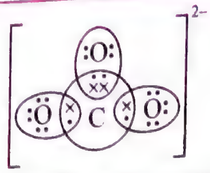
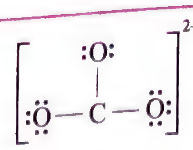
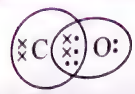
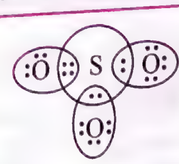
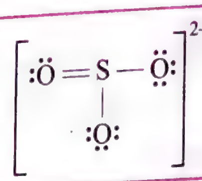
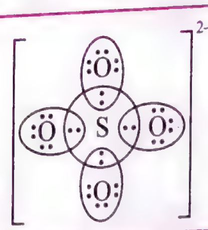
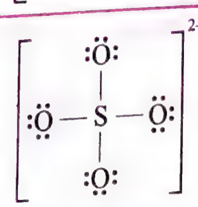
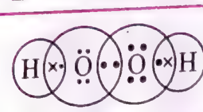
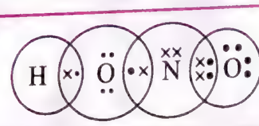
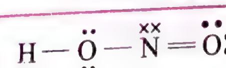
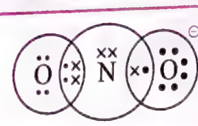
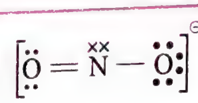
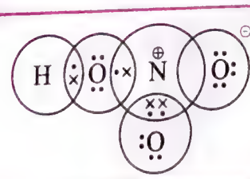
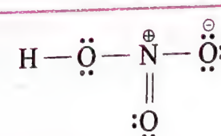
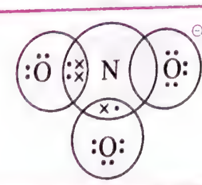
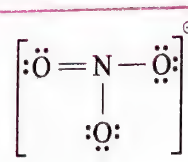
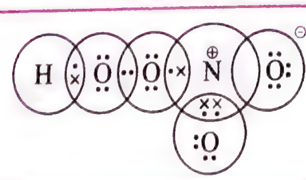
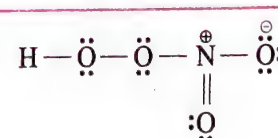
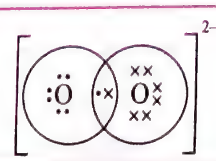
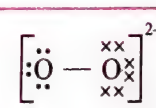
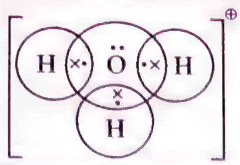
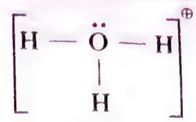
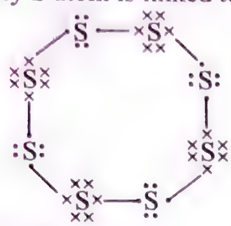
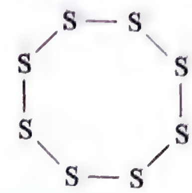
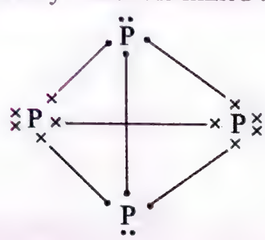
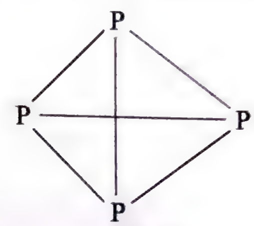
or 

Table 2.2 The Lewis representation of some molecules

1.	H_2		H • • H
2.	O_2		
3.	O_3		

4.	NF_3	 (×) e^- on F and (.) e^- on O	
5.	CO_3^{2-}	 (×) e^- on C and (•) e^- on O.	
6.	CO	 (×) e^- on C and (•) e^- on O	
7.	SO_3^{2-}		
8.	SO_4^{2-}		
9.	H_2O_2 (Hydrogen peroxide)		
10.	HNO_2 (Nitrous acid)		
11.	$NO_2^{\ominus}$ (Nitrite ion)		
12.	HNO_3 (Nitric acid)		
13.	$NO_3^{\ominus}$		
14.	HNO_4 (Per-oxonitric acid)		
15.	O_2^{2-} (Peroxide ion)		

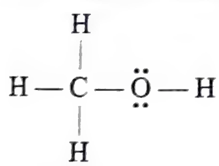
16.	$H_3O^{\oplus}$ (Hydronium ion)		
17.	S_8	Every S atom is linked to 2 other S atoms by single covalent bond.  or 	
18.	P_4	Every P atom is linked to 3 other P atoms by single covalent bond.  or 	

2.11 FORMAL CHARGE

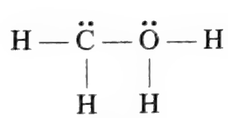
It is possible to represent two different Lewis structures for a molecule that differs in the arrangement of at atoms, e.g. a molecule X_2Y can be represented as:

$$X—X—Y \quad \text{or} \quad X—Y—X.$$

Sometimes both structures represent real compounds that are isomers of each other. More often, only one structure exists in nature. For example, methanol can be written in two ways:



(a)



(b)

The structure (b) does not correspond to any real compound even through it obeys octet rule.

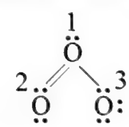
There are several ways to choose the more correct of the two structures, the one involves a concept called *formal charge*, which can be applied to any atom within a Lewis structure.

Generally, the Lewis dot structure does not represent the actual shapes of the molecules. Although in the case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom, for some purposes a formal charges (FC) is assigned to each atom. The formal charge of an atom in a polyatomic ion/molecule is defined as:

$$\text{Formal charge (FC) on an atom in a Lewis structure} = \begin{bmatrix}\text{Total number of}\\ \text{valence electrons}\\ \text{in the free atom}\end{bmatrix} - \begin{bmatrix}\text{Total number}\\ \text{of non-bonding}\\ \text{(lone pair electrons)}\end{bmatrix} - 1/2 \begin{bmatrix}\text{Total number of}\\ \text{bonding (shared}\\ \text{electrons)}\end{bmatrix}$$

The formal charge is the difference between the number of valence electrons in an isolated (i.e. free) atom and the number of electrons assigned to that, in a Lewis structure.

The counting being based on the assumption, that the atom in the molecule owns one electron of each shared pair and both the electrons of a lone pair. For example, in O_3, the central O atom is bonded to two other O atoms in the arrangement shown below:



Using the relationship given above, the formal charge on the O atoms is calculated as follows:

1. **The central O atom marked 1:** The central atom marked 1 has six valence electrons, one lone pair (or two non-bonding electrons) and three bonds (or six bonding). Therefore its formal charge is

   $$6 - 2 - \frac{1}{2}(6) = +1$$

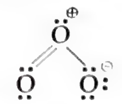
2. **The end O atom marked 2:** This atom has six valence electrons, two lone pairs (or 4 non-bonding electrons) and two bonds (or 4 bonding electrons). Therefore its formal charge is

   $$6 - 4 - \frac{1}{2}(4) = 0$$

3. **The end O atom marked 3:** This atom has six valence electrons, three lone pairs (or six non-bonding electrons) and one bond (or two bonding electrons). Thus, its formal charge is

   $$6 - 6 - \frac{1}{2}(2) = -1$$

Therefore the formal charges on the oxygen atoms in the Lewis structures of O_3 given above are written as:



The formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species.

Generally, the lowest energy structure is the one, with the smallest formal charges on the atoms. The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.

Note: The sum of the formal charges on the atoms in a molecule or ion is always equal to its net charge.

Examples:

a. In O_3 molecule (refer to the example in Section 2.11)
FC on O-atom (marked 1) = +1
FC on O-atom (marked 2) = 0
FC on O-atom (marked 3) = –1
The sum of FC = 0 and new charges on O_3 = 0.
This shows that there is no charge on the O_3 molecule but the FC's on the O-atoms (marked 1 and 2) is +1 and –1. respectively.

b. Hydroxide ion ($\overset{\ominus}{O}H$):

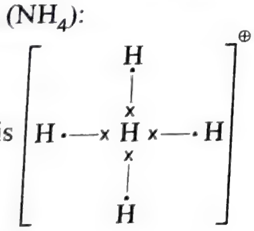
Lewis structure is $\left[:\overset{\ominus}{\ddot{\underset{\cdot\cdot}{O}}}\cdot\!\!-\!\!\times H\right]$

$$\text{FC on O-atom} = 6 - 6 - \frac{1}{2}(2) = -1$$

$$\text{FC on H-atom} = 1 - 0 - \frac{1}{2}(2) = 0$$

The sum of F.C = –1. The net charge on the ion = –1.

c. Ammonium ion ($\overset{\oplus}{N}H_4$):

Lewis structure is 

$$\text{FC on N-atom} = 5 - 0 - \frac{1}{2}(8) = +1.$$

$$\text{FC on every H-atom} = 1 - 0 - \frac{1}{2}(2) = 0.$$

The sum of FC = +1. Net charge on the ion = +1.

2.11.1 Applications of FC's to Resonance Structures

The two or more resonance structures of a compound are not identical, one of the structure may be better than the others means that it is more close to the actual electronic structure of the compound. For example, the two resonance structures (a) and (b) of N_2O (nitrous oxide) molecule are:

(a) (b)

In structure (a):

$$\text{FC on O-atom} = 6 - 6 - \frac{1}{2}(2) = -1$$

$$\text{FC on N}^1\text{-atom} = 5 - 0 - \frac{1}{2}(8) = +1$$

$$\text{FC on N}^2\text{-atom} = 5 - 2 - \frac{1}{2}(6) = 0$$

In structure (b):

$$\text{FC on O-atom} = 6 - 4 - \frac{1}{2}(4) = 0$$

$$\text{FC on N}^1\text{-atom} = 5 - 0 - \frac{1}{2}(8) = +1$$

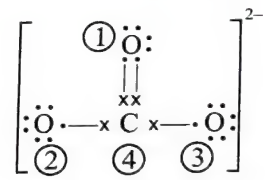
$$\text{FC on N}^2\text{-atom} = 5 - 4 - \frac{1}{2}(4) = -1$$

Since O-atom is more EN than N-atom, the structure (a) favourable resonance structure of N_2O.

ILLUSTRATION 2.4

Calculate the formal charge on atoms in carbonate (CO_3^{2-}).

Sol. Lewis structure of CO_3^{2-} ion is



a. Formal charge on C-atom:
No. of valence e^- on C (marked 4) = 4 e^-'s
Lone pair (lp) electrons on C = 0
No. of bonds C atom forms = 4
No. of bonding e^-'s = 4 × 2 = 8 e^-'s

$$FC = \begin{bmatrix}\text{No. of} \\ \text{valence } e^-\text{'s}\end{bmatrix} - \begin{bmatrix}\text{No. of} \\ lp\ e^-\text{'s}\end{bmatrix} - \frac{1}{2}\begin{bmatrix}\text{No. of} \\ \text{bonding } e^-\text{'s}\end{bmatrix}$$

$$\therefore \text{FC on C-atom} = 4 - 0 - \frac{1}{2}(8) = 0.$$

b. FC on O-atom marked 1:
No. of valence e^- on O-atom (marked 1) = 6e^-'s
Lone pair (lp) electrons on O-atom = 2 × 2 = 4 e^-'s
No. of bonds O-atom forms = 2
No. of bonding e^-'s = 2 × 2 = 4 e^-'s

$$\text{Hence, FC on O-atom (marked 1)} = 6 - 4 - \frac{1}{2}(4) = 0.$$

c. FC on O-atom (marked 2):
No. of valence e^- on O-atom = 6 e^-'s

Lone pair electrons (lp) on O-atom $= 3 \times 2 = 6\ e^-$'s
No. of bonds O-atom forms = 1
No. of bonding e^-'s $= 2 \times 1 = 2\ e^-$'s

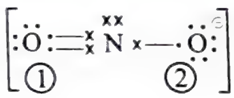
d. FC on O-atom (marked 3) $= 6 - 6 - \frac{1}{2}(2) = -1$
(Same as in part c.)

e. Sum of FC's = Net charge on $CO_3^{2-} = -2$

ILLUSTRATION 2.5

Calculate the formal charge on each atoms in nitrite ion.

Sol. Lewis structure of $NO_2^{\ominus}$ ion is



a. FC on N-atom:
No. of valence e^- on N-atom $= 5\ e^-$'s
Lone pair (lp) electrons on N-atom $= 1 \times 2 = 2\ e^-$'s
No. of bonds N-atom forms = 3
No. of bonding e^-'s $= 3 \times 2 = 6\ e^-$'s

Hence, FC on N-atom $= 5 - 2 - \frac{1}{2}(6) = 0.$

b. FC on O-atom (marked 1):
No. of valence e^- on O-atom $= 6e^-$'s
Lone pair (lp) electrons on O-atom $= 2 \times 2 = 4e^-$'s
No. of bonds O-atom forms = 2
No. of bonding e^-'s $= 2 \times 2 = 4e^-$'s

Hence, FC on O-atom (marked 1) $= 6 - 4 - \frac{1}{2}(4) = 0.$

c. FC on O-atom (marked 2):
No. of valence e^- on O-atom $= 6e^-$'s
Lone pair (lp) electrons on O-atom $= 3 \times 2 = 6$
No. of bonds O-atom forms = 1
No. of bonding e^-'s $= 1 \times 2 = 2e^-$'s

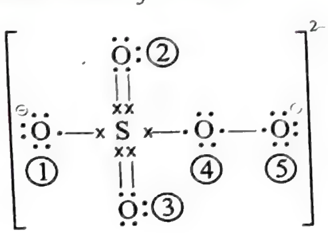
Hence, FC on O-atom (marked 2) $= 6 - 6 - \frac{1}{2}(2) = -1.$

d. Sum of FC's = Net charge of $NO_2^{\ominus} = -1.$

ILLUSTRATION 2.6

Calculate the formal charge on each atom in SO_5^{2-} (per-oxosulphate ion).

Sol. Lewis structure of SO_5^{2-} ion is



a. FC on S-atom:
No. of valence e^- on S-atom $= 6\ e^-$'s
Lone pair (lp) electrons on S-atom = 0
No. of bond pair e^-'s S-atom forms $= 6 \times 2 = 12\ e^-$'s

FC on S-atom $= 6 - 0 - \frac{1}{2} \times (12) = 0$

b. FC on O-atom (marked 1 and 5):
No. of valence e^- on O-atom $= 6\ e^-$'s
Lone pair e^-'s on O-atom $= 3 \times 2 = 6e^-$
No. of bond pair e^-'s on O-atom $= 2e^-$

FC on O-atom (marked 1 and 5) $= 6 - 6 - \frac{1}{2} \times 2$

$= \begin{bmatrix} -1 \text{ on each} \\ \text{O-atom or } -2 \\ \text{on both O-atoms} \end{bmatrix}$

c. FC on O-atom (marekd 2 and 3) is

$6 - 4 - \frac{1}{2} \times 4 = 0$

d. FC on O-atom (marked 4) is

$6 - 4\ \frac{1}{2} \times 4 = 0$

Therefore, sum of FC $= 0 - 2 + 0 = -2$

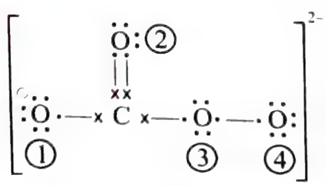
Net charge on $SO_5^{2-} = -2$

Hence, sum of FC = Net charge on the ion

ILLUSTRATION 2.7

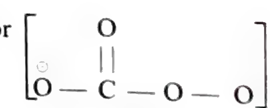
Calculate the formal charge on each atom in CO_4^{2-} (per-oxocarbonate ion).

Sol. Lewis structure of CO_4^{2-} ion is



Lewis dot formula

or



Dash formula

a. FC on C-atom $= 4 - 0 - \frac{1}{2}(8) = 0$

b. FC on O-atoms (marked 1 and 4) $= 6 - 6 - \frac{1}{2} \times 2$

$= -1 \begin{bmatrix} \text{on each O-atom} \\ \text{or } -2 \text{ on both} \\ \text{O-atoms} \end{bmatrix}$

c. FC on O-atoms (marked 2 and 3) $= 6 - 4 - \frac{1}{2} \times 4$
$= 0$

d. Sum of FC's = Net charge on $CO_4^{2-} = -2$

2.12 ISOSTERES

Molecules or polyatomic ions containing same number of atoms and the same total numbers of electrons are called *isosteres*. Generally, isosteres have identical Lewis structures, e.g., CO, N_2 and $CN^{\ominus}$ are isosteres.

Each of them contains 2 atoms and 14 e^-'s (same total number of electrons). Their Lewis structures are identical as shown:

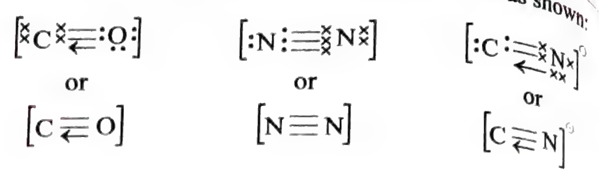


Table 2.3 Some examples of isosteric species

	Isosteric species	No. of atoms	No. of electrons	No. of valence electrons in each atom or ion
1.	CO_2, N_2O, $\overset{\oplus}{NO_2}$, $CN\overset{\ominus}{O}$	3	$\left[\begin{array}{l} CO_2 = 6+16 \\ N_2O = 14+8 \\ \overset{\oplus}{NO_2} = 7+16-1 \\ CN\overset{\ominus}{O} = 6+7+8+1 \end{array}\right] = 22$	$\left[\begin{array}{l} CO_2 = 4+6\times 2 \\ N_2O = 5\times 2+6 \\ \overset{\oplus}{NO_2} = 5+6\times 2-1 \\ C\overset{\ominus}{N}O = 4+5+6+1 \end{array}\right] = 16$
2.	$NO_3^{\ominus}$, BO_3^{3-}, CO_3^{2-}	4	32	24
3.	$ClO_3^{\ominus}$, SO_3^{2-}	4	42	26
4.	PO_4^{3-}, $ClO_4^{\ominus}$	5	50	32
5.	CH_4, $\overset{\oplus}{NH_4}$	5	10	8
6.	$MnO_4^{\ominus}$, CrO_4^{2-}	5	58	32
7.	$H_3O^{\oplus}$, NH_3	4	10	8

2.13 BOND ENTHALPY OR BOND DISSOCIATION ENTHALPY

It is defined as the amount of energy required to break one mole of bonds of a compound in gaseous state to its constituent gaseous atoms. The unit of bond enthalpy is KJ mol^{-1}.

Examples:

1. **For diatomic molecules:**

   a. $H_{2(g)} \longrightarrow 2H_{(g)}$, $\quad \Delta_a H^{\ominus} = 435.8$ kJ mol^{-1}

   b. $O_2\,(O=O)_{(g)} \longrightarrow 2\,O_{(g)}$, $\quad \Delta_a H^{\ominus} = 498$ kJ mol^{-1}

   c. $N_2\,(N\equiv N)_{(g)} \longrightarrow 2\,N_{(g)}$, $\quad \Delta_a H^{\ominus} = 946.0$ kJ mol^{-1}

2. **For a heteronuclear diatomic molecules:**

   $HCl_{(g)} \longrightarrow H_{(g)} + Cl_{(g)}$, $\quad \Delta_a H^{\ominus} = 431.0$ kJ mol^{-1}

Note: The larger the bond dissociation enthalpy, the stronger is the bond in the molecule.

3. **For polyatomic molecules:** In such cases, the measurement of bond strength is more complicated, e.g. in case of H_2O molecule, the enthalpy needed to break the two O–H bonds is not the same.

$H_2O_{(g)} \longrightarrow H_{(g)} + OH_{(g)}$: $\quad \Delta_a H_1^{\ominus} = 502$ kJ mol^{-1}

$OH(g) \longrightarrow H(g) + O(g)$: $\quad \Delta_a H_1^{\ominus} = 427$ kJ mol^{-1}

The difference in the $\Delta_a H^{\ominus}$ value shows that the second O–H bond undergoes some changes because of changed chemical environment. This is the reason for some difference in energy of the same O–H bond in different molecules such as C_2H_5OH (ethanol) and water. Therefore, in polyatomic molecules the term **mean average bond enthalpy** is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken as explained below in case of water molecule.

$$\text{Average bond enthalpy} = \frac{502+427}{2} = 464.5 \text{ kJ mol}^{-1}$$

Note: For factors affecting bond enthalpy, refer to Chapter 1.

2.14 BOND ORDER

In the Lewis description of covalent bond, the bond order is given by the number of bonds between the two atoms in a molecule. The bond order, for example in H_2 (with a single shared electron pair), in O_2 (with two shared electron pairs) and in N_2 (with three shared electron pairs) is 1, 2, 3 respectively. Similarly, in CO (three shared electron pairs between C and O) the bond order is 3. For N_2, bond order is 3 and its $\Delta_a H^{\ominus}$ is 946 kJ mol^{-1}; being one of the highest for a diatomic molecule.

Isoelectronic molecules and ions have identical bond orders; for example, F_2 and O_2^{2-} have bond order 1. N_2, CO and $NO^{\oplus}$ have bond order 3.

A general correlation useful for understanding the stabilities of molecules is that: with increase in bond order, bond enthalpy increases and bond length decreases.

Note: For other bonding parameters, such as bond length, types of atomic radii, bond length and lattice enthalpy, refer to Chapter 1.

2.15 RESONANCE STRUCTURES

It is observed oftenly that a single Lewis structure does not represent a molecule in agreement with its experimentally determined parameters.

For example, O_3 (ozone) molecule can be equally represented by the structures I and II shown below:

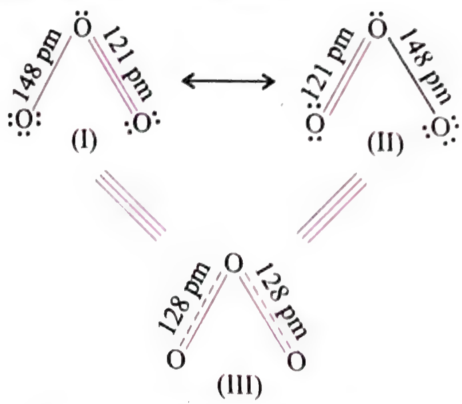


Fig. 2.5 Resonance in the O_3 molecule

Structures I and II represent the two canonical forms while structure III is the resonance hybrid.

In both structures, we have a O–O single bond and a O=O double bond. The normal O–O and O=O bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen–oxygen bond lengths in the O_3 molecule are same (128 pm). Thus, the oxygen bonds in the O_3 molecule are intermediate between a double and a single bond. Obviously, this cannot be represented by either of the two Lewis structures shown above.

Therefore, concert of resonance was introduced to explain the accurate structure of molecules like O_3.

Definition of resonance

Whenever a single Lewis structure cannot explain all the properties of a molecule accurately. The molecule is then supposed to have many structures with similar energy, position of nuclei, bonding and non-bonding pairs of electrons.

Each of these structures can explain most of the properties of the molecule but cannot explain all the properties of the molecule. The actual structure is in between these resonating structures and is called *resonance hybrid* and the different individual structures are called *resonating structures* or *canonical forms*. This phenomenon is called *resonance*.

For O_3, the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e. structure III represents the structure of O_3 more accurately and is called *resonance hybrid.*

2.15.1 Conditions of Resonating Structures

The different resonating structures of a substance have:

1. Same position of atoms.
2. Same number of paired and unpaired electrons.
3. Almost equal energy.
4. They differ only in the arrangement of electrons in different resonating forms. Resonance structures are represented by a double headed arrow (↔).

2.15.2 Possibility of Resonance

1. Two or more double bonds or two or more triple bonds or one double or triple bonds are in conjugation, e.g.,

   a. $H_2C=CH-CH=CH_2 \leftrightarrow \overset{\oplus}{C}H_2-CH=CH-\overset{\ominus}{C}H_2$
   (Buta-1, 3-diene)
   (conjugated diene)

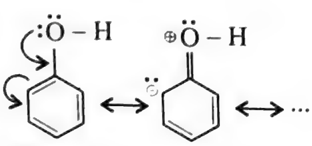
   b. $H_2C=C=CH_2$ ↔ [No resonance is possible, because double bonds are not in conjugation.]
   (Prop-1, 2-diene)
   (cumulative diene)

   c. $H_2C=CH-CH_2-CH=CH_2$ ↔ [Resonance is not possible, because double bonds are not in conjugation.]
   (Penta-1, 4-diene)
   (isolated diene)

   d. $HC\equiv C-CH=CH_2 \leftrightarrow H\overset{\oplus}{C}=C=CH-\overset{\ominus}{C}H_2$
   (Butan-1-en-3-yne)

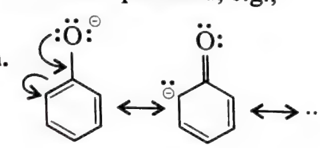
2. Lone pair of electrons (i.e. non-bonding electrons) is in conjugation with double or triple bond, e.g.,

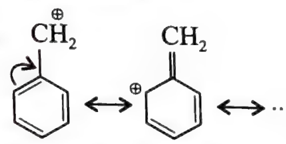
   a. $CH_2=CH-\ddot{\underset{..}{Cl}}: \leftrightarrow \overset{\ominus}{C}H_2-CH=\overset{\oplus}{Cl}:$
   (Vinyl chloride)

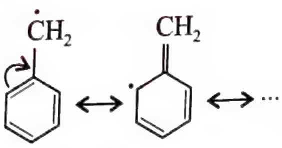
   b. 
   (Phenol)

   c. $CH_2=CH-CH_2-\ddot{\underset{..}{Cl}}:$ ↔ [Resonance is not possible, because *lp* of e^-'s are not in conjugation with double bonds.]
   (Allyl chloride)

3. Negative or positive or free radical is in conjugation with double or triple bond, e.g.,

   a. 
   (Phenoxide ion)

   b. 
   (Benzyl carbocation)

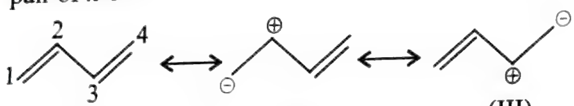
c. 

(Benzyl radical)

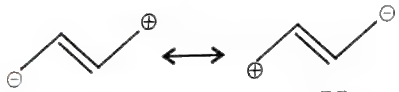
In general, it may be stated that (i) Resonance stabilises the molecule as the energy of the resonance hybrid is less than the energy of any single cannonical structure; and (ii) Resonance averages the bond characteristics as a whole. Thus the energy of the O_3 resonance hybrid is lower than either of the two cannonical forms I and II (Fig. 2.5).

Some more examples of resonance are as follows:

In buta-1,3-diene (I), the ($C_1 — C_2$) and ($C_3 — C_4$) bonds are found to be longer than ($C = C$) bond, and ($C_2 — C_3$) bond is slightly shorter than a ($C — C$) bond. This can be explained by writting several other structures by shifting a pair of π-e–'s.



(I) (II) (III)



(IV) (V)

The structures (II) and (III) show partial single-bond character of ($C_1—C_2$) and ($C_3—C_4$) bonds. The structures (IV) and (V) show partial double bond character of ($C_3 — C_4$). This explains the observed anomalies in the bond distance in the hybrid. Thus, in the real structure (i.e., hybrid structure) of the compound, lateral overlap of all the four *p*-orbitals has taken place, i.e., delocalisation of e^-'s has occurred which imparts stability to it, as shown in Fig. 2.6.

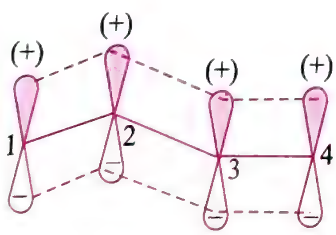


Fig. 2.6 Lateral overlap of p orbitals in the hybrid structure

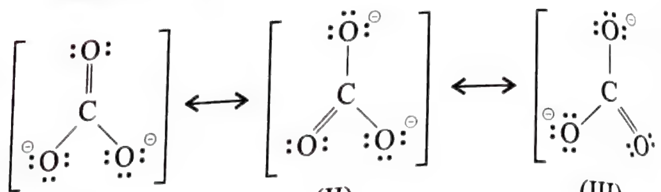
Here, (+) and (–) are not charges, but represent phases of waves. Waves of same phases overlap effectively.

ILLUSTRATION 2.8

a. Explain the structure of CO_3^{2-} ion in terms of resonance.
b. Explain the resonance structures of CO_2 molecule.

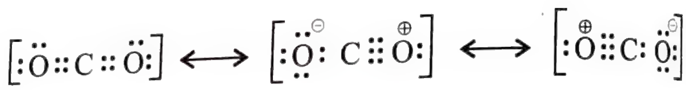
Sol.

a. The single Lewis structure based on the presence of two single bonds and one double bond between carbon and oxygen atoms is inadequate to represent the molecule accurately as it represents unequal bonds. According to the experimental findings, all carbon to oxygen bonds in CO_3^{2-} are equivalent. Therefore, the carbonate ion is best described as a resonance hybrid of the canonical forms I, II and III shown below.



(I) (II) (III)

b. The experimentally determined carbon to oxygen bond length in CO_2 is 115 pm. The lengths of a normal carbon to oxygen double bond (C = O) and carbon to oxygen triple bond (C ≡ O) are 121 pm and 110 pm respectively. The carbon–oxygen bond lengths in CO_2 (115 pm) lie between the values for C = O and C ≡ O. Obviously, a single Lewis structure cannot depict this position and it becomes necessary to write more than one Lewis structures and to consider that the structure of CO_2 is best described as a hybrid of the canonical or resonance forms I, II and III shown below.



(I) (II) (III)

2.15.3 Resonance Energy

The resonance hybrid is more stable than any of the contributing structures. In other words, the resonance hybrid has lower energy than any of the contributing structures.

The difference in the energy of the resonance hybrid and the most stable contributing structure (having least energy) is called resonance energy (RE) (or) the difference in the experiment and calculated enthalpies (bond enthalpy, formation, combustion, or hydrogenation enthalpies) is called RE (Fig. 2.7). This is the amount of energy by which the compound is stable. The RE of buta-1,3-diene and benzene were found to be about 16.72 and 150.0 kJ mol^{-1}, respectively.

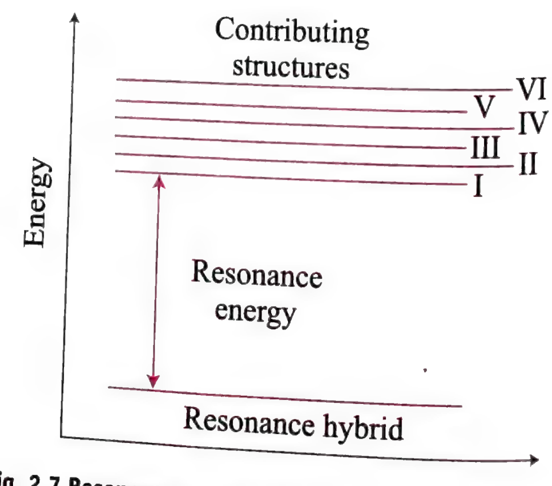
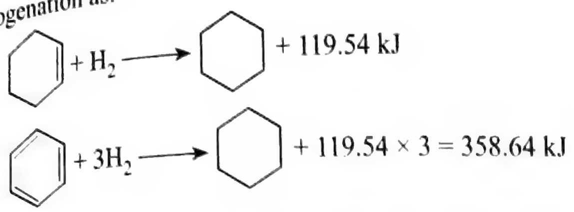


Fig. 2.7 Resonance energy of the contributing structures

The RE of benzene has been calculated from the heat of hydrogenation as:



If hypothetically, benzene is cyclohexatriene (containing three (C=C) bonds), the heat of hydrogenation should be −358.64 kJ. But experimentally, it was found to be 208.64 kJ mol^{-1}, i.e. benzene evolves [(−358.64)−(208.64)] = 150 kJ mol^{-1} less energy than anticipated for the hypothetical cyclohexatriene. Therefore, the RE of benzene (150 kJ mol^{-1}) is due to the delocalisation of π-e^-'s in a cyclic molecular model.

Characteristics of resonance: The necessary conditions of resonance are as follows:

1. All resonating structures must have the same arrangement of atomic nuclei.
2. The resonating structures must have the same number of paired or unpaired e^-'s. However, they differ in the way of distribution of e^-'s. $\dot{C}H_2-CH=CH-\dot{C}H_2$ is not considered a resonance structure of buta-1,3-diene.
3. All the resonating structures have same total charge.
4. The energies of various structures must be same or nearly same.

Main characteristics:

1. It gives identical bonding (concept of partial double bond in resonance hybrid) and hence identical bond length. For example, in benzene, all (C—C) bond lengths are of 139 pm each.

   [Intermediate values of (C — C) and (C = C) bonds, (C—C) ⇒ 154 pm, (C=C) ⇒ 134 pm]
2. It leads to the shortening of single C — C or other bonds in resonance hybrid.
3. Due to the spreading of π-e^-'s (delocalisation) throughout the surface of the molecule, it induces stability in the molecule as a whole. Hence, the molecules showing resonance are less reactive.
4. **a.** Non-polar structures are more stable than dipolar.

   b. Resonance structures with a greater number of covalent bonds are more stable than those with lesser number. Thus, non-polar structure (I) of buta-1,3-diene is more stable than any other resonating structures.

   c. Resonance structures with similar charges on adjacent atoms are insignificant due to electrostatic repulsion and thus are unstable, e.g. $\overset{\oplus}{C}H_2-\overset{\ominus}{C}H-\overset{\ominus}{C}H-\overset{\oplus}{C}H_2$. This resonance form does not contribute to the stability of the hybrid.

   d. Structures with positive charge on electropositive element and negative charge on electronegative element are more stable. For example,

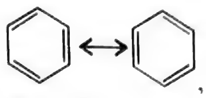
$$>C=O \longleftrightarrow >\overset{\oplus}{C}-\overset{\ominus}{O}$$

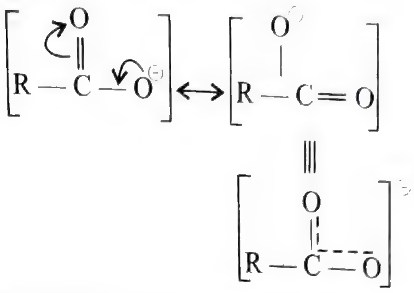
Stable form

$$>C=O \longleftrightarrow >\overset{\ominus}{C}-\overset{\oplus}{O}$$

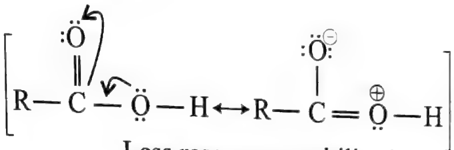
Unstable form

   e. When there are two equivalent structures, resonance stabilisation is the greatest. For example,

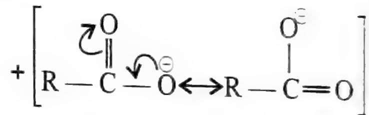
i. 

ii. 

   f. Structures in which charge delocalised are more stable than those in which there is charge separation. For example,



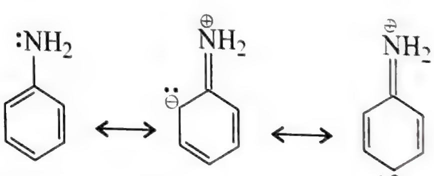
Less resonance stabilised



More resonance stabilised

Hence, carboxylic acid favours ionisation.

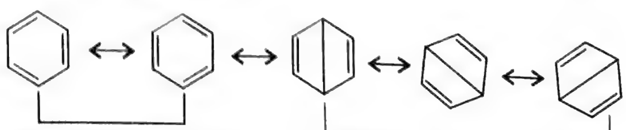
   g. Structures in which there is less separation of opposite charges are more stable than those with more charge separation. For example,



(Neutral) (I) | (Less charge separation) (II) | (More charge separation) (III)

Stability order: I > II > III

   h. The individual structures of similar energy contribute equally to the resonance hybrid canonical structures with somewhat higher energy may also contribute to the resultant hybrid, but the higher the energy of a particular structure, the lesser is its contributions. For example, the canonical forms of benzene are:



Two equivalent Kekule forms (Lower energy)

(Three equivalent Dewar forms) (Higher energy)

Contribution from the two equivalent lower energy Kekulé forms is more as compared to the contribution from the three equivalent Dewar higher energy canonical forms to the resonance hybrid benzene.

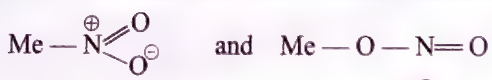
i. All the atoms in a molecule taking part in resonance should be coplanar. Because this enables effective overlap of p-orbitals and delocalisation of the e^-'s. Moreover, resonance structures with $2p$–$2p$ overlap is much more stable than $2p$–$3p$ or $2p$–$4p$ or $3p$–$4p$, etc. overlaps.

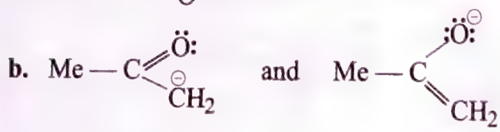
Misconception associated with resonance:

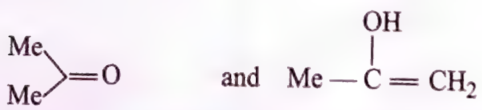
1. The canonical forms have no real existence.
2. The molecule does not exist for a certain fraction of time in one canonical form and for other fractions of time in another canonical forms.
3. No equilibrium exists between the canonical forms as between tautomeric keto and enol forms in tautomerism.
4. The molecule as such has a single structure which is the resonance hybrid of the canonical forms and which cannot as such be represented by a single Lewis structure.

ILLUSTRATION 2.9

Which of the following pairs do not constitute resonance structures?

a. 

b. 

c. 

d. Me CH $=$ CH Me and Me CH_2 CH $=$ CH_2

Sol.

a. In resonance, the position of atoms or nuclei remains fixed, so pairs in (b) constitute resonance. In other pairs, the positions of atoms are changing; therefore, (a), (c), and (d) pairs do not constitute resonance structures.

a. They constitute functional isomerism (nitro to nitrite).

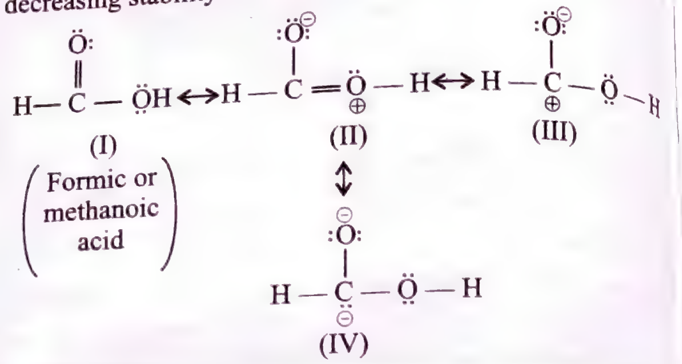
b. They constitute resonance structures.

c. They constitute tautomerism (keto and enol) and also show functional isomerism.

d. They constitute positional isomerism (position of double bond has changed).

ILLUSTRATION 2.10

Arrange the following resonating structures in the order of decreasing stability.



Sol.

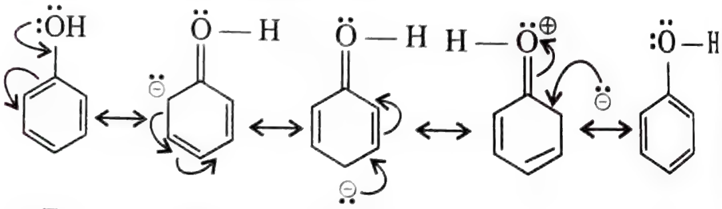
a. Structures (I) and (II) have greater number of covalent bonds; hence, these are more stable than either (III) or (IV). Furthermore, between I and II, structure I has no formal charges and hence is more stable than structure (II).

b. Structure (IV) is less stable than (III) because in (IV) the positive charge is on oxygen, which is a more EN atom than carbon on which positive charge is present in (III). Thus, the order of stability is I > II > III > IV.

ILLUSTRATION 2.11

Write the resonance structure of phenol in order of decreasing stabilities.

Sol. In the resonating structure of phenol as shown below, structures (I) and (V) are more stable than the others. Structures (III), (IV) and (V) are less stable due to charge separation and positive charge on oxygen atom.



(I) (II) (III) (IV) (V)

Order of stability $\Rightarrow$ (I) = (V) > (II) = (IV) > (III)

(I) and (V) $\Rightarrow$ Uncharged structures

(III) $\Rightarrow$ More charge separation

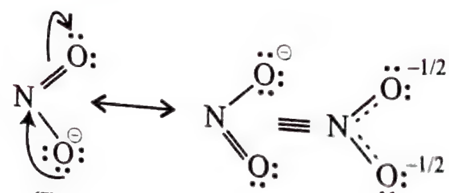
Order of energy $\Rightarrow$ (III) > (II) = (IV) > (I) = (V)

(II) and (IV) $\Rightarrow$ Less charge separation

ILLUSTRATION 2.12

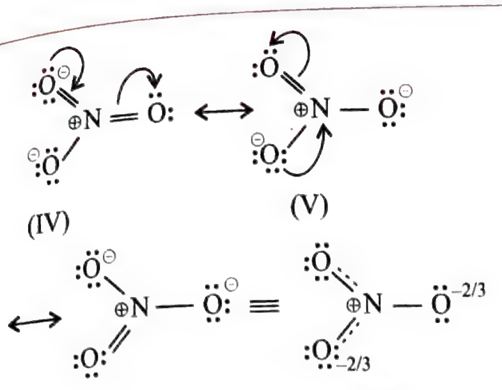
Write the resonance structures of $NO_2^{\ominus}$ (nitrite) and $NO_3^{\ominus}$ (nitrate ion).

Sol.

a. $NO_2^{\ominus}$: 

(I) (II) (III) (Hybrid)

b. $NO_3^{\ominus}$:



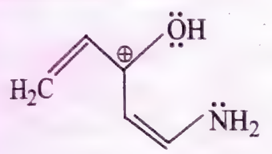
(IV) (V) (VI) (VII)

In the resonance hybrid structures, dashed-line bonds are used to indicate double or triple bond character between the bonded atoms. These partial multiple bonds represent the extended π-bond overlap. In each resonance contributing structures, the negative charge resides on a different O atom. But in the hybrid structures, each O atom has a fractional negative charge.

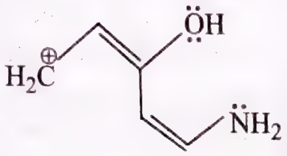
ILLUSTRATION 2.13

Which of the following is the most stable resonance structure?

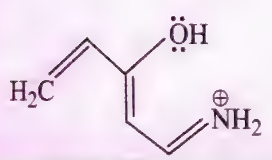
a.



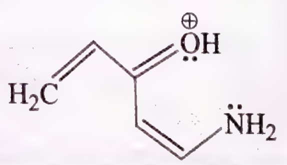
b.



c.



d.



Sol.

c. Structure (c) is the most stable resonance structure.

i. Number of covalent bonds in (a) and (b) = 13.

ii. Number of covalent bonds in (c) and (d) = 14.

iii. In (c), positive charge is on N, whereas in (d), it is on O atom. Since N is less EN (electronegative) than O, (c) is more stable.

iv. Order of stability: c > d > a > b.

ILLUSTRATION 2.14

Give the stability order of the following resonance structures:

a. $H_2C=\overset{\oplus}{N}=\overset{\ominus}{N}$ b. $H_2\overset{\oplus}{C}-N=\overset{\ominus}{N}$

c. $H_2\overset{\ominus}{C}-\overset{\oplus}{N}\equiv N$ d. $H_2\overset{\ominus}{C}-N=\overset{\oplus}{N}$

Sol.

a. The lesser the charge separation, the more stable the resonating structure. Structures (I) and (III) have less charge separation. But in (III), charge is on electropositive C atom. Therefore, (I) is more stable than (III). Since both have six covalent bonds, so (I) is more stable than (III) (I > III).

b. Both structures (II) and (IV) have five covalent bonds, but (II) is more stable than (IV) because in (II) positive charge is on electropositive C atom and negative charge is on EN (electonegative) N atom, whereas in (IV) it is reversed. Therefore, II > IV. So, the stability order is I > III > II > IV.

2.16 POLARITY OF COVALENT BOND, POLARISABILITY AND FAJANS' RULE

A polar covalent bond results when a bond is formed between atoms having a large difference in EN values. A non-polar covalent bond results between atoms having a very small or zero difference in EN values. The polarity of covalent bond, polarisability and Fajans' rule have already been discussed in Chapter 1.

In reality, no bond or a compound is completely covalent or ionic. Even in case of covalent bond between two H atoms, there is some ionic character.

Just as all the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character. The partial covalent character of ionic bonds is explained by *Fajans' rule* in terms of the following conditions.

The covalent character is greater when (i) the cation is small, (ii) the anion is large and (iii) there is a high charge on the ions. For cations having same size and charge, the one with electronic configuration $(n-1)d^n ns^0$ (typical of transition metals) is more covalent (polarising) than the one with a noble gas configuration, $ns^2\, np^6$, typical of alkali and alkaline earth metals.

The cation polarises the anion, pulling the electronic charge towards itself and thereby increasing the electronic charge between the two.

To sum up, the polarising power of the cation, the polarisability of the anion, and the extent of distortion (polarisation) of anion are the factors which determine the per cent covalent character of the ionic bond.

Examples:

1. LiCl, NaCl, KCl, RbCl, CsCl

   Size of cation is the deciding factor (charge of each ion and size of Cl is same)

   $Li^{\oplus} < Na^{\oplus} < K^{\oplus} < Rb^{\oplus} < Cs^{\oplus}$

   $\longrightarrow$ Size of cation

   $\longleftarrow$ Polarisation

   LiCl > NaCl > KCl > RbCl > CsCl

   $\longleftarrow$ Covalent character

   $\longrightarrow$ m.pt, and b.pt

   $\longrightarrow$ Conductivity

   $\longrightarrow$ Solubility in H_2O (polar solvents)

   $\longleftarrow$ Solubility in non-polar solvent

2. NaF, NaCl, NaBr, NaI

Deciding factor is the size of the anion. Larger the size of the anion, greater the polarisation hence greater the covalent nature.

$$\xrightarrow[\text{Size of anion}]{F^{\ominus} < Cl^{\ominus} < Br^{\ominus} < I^{\ominus}}$$

$$\xrightarrow[\text{Polarisation}]{F^{\ominus} < Cl^{\ominus} < Br^{\ominus} < I^{\ominus}}$$

$$\xrightarrow[\text{Covalent nature}]{NaF < NaCl < NaBr < NaI}$$

3. NaCl, $MgCl_2$, $AlCl_3$, $SiCl_4$, PCl_5

$$\xleftarrow[\text{Size of cation}]{Na^{\oplus} > Mg^{2+} > Al^{3+} > Si^{4+} > P^{5+}}$$

$$\xrightarrow[\text{Charge on cation}]{}$$

Note: Greater the charge, smaller the size, then greater the polarisation.

$$\xrightarrow[\text{Polarisation}]{Na^{\oplus} < Mg^{2+} < Al^{3+} < Si^{4+} < P^{5+}}$$

$$\xrightarrow[\text{Covalent nature}]{NaCl < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5}$$

4. NaF, Na_2O, Na_3N

$\xrightarrow{F^{\ominus} < O^{2-} < N^{3-}}$ Size of anion

$\xrightarrow{F^{\ominus} < O^{2-} < N^{3-}}$ Charge on anion

$\xrightarrow{F^{\ominus} < O^{2-} < N^{3-}}$ Polarisation

$\xrightarrow{NaF < Na_2O < Na_3N}$ Covalent nature

5. CuCl and NaCl

$[Cu^{\oplus}]$ $[Ar]3d^{10}$

$[Na^{\oplus}]$ $[Ne]$

Cations with 18-electron shells have greater polarising power than the 8-electron shell ions with the same charge and size. This is due to the increased electronegativity of the 18-electron shell ions as the inner electrons have poor shielding affect on the nucleus. Thus, CuCl is covalent and NaCl is ionic.

2.17 DIPOLE MOMENTS (μ)

It is the vector sum of all the individual bond moments. Mathematically, $\mu = q \times d$, where q is the magnitude of partial charges and d is the distance between the centres of opposite charge.

The charge q is of the order of 10^{-10} esu and d is the order of 10^{-8} cm (1 Å). Therefore, the dipole moment (μ) is the order of $10^{-10} \times 10^{-8} = 10^{-18}$ esu cm. This quantity is known as one *debye* (denoted by the symbol D).

1 D = 10^{-18} esu cm

If q is in coulomb and d is in metre (m), then μ is expressed in coulomb metre (C.m).

1 D = 3.33564×10^{-30} C.m

In SI units,

$$\text{As 1 esu} = \frac{1.602 \times 10^{-19}\,C}{4.803 \times 10^{-10}}$$

$$= 3.335 \times 10^{-10}\,C$$

and 1 cm = 10^{-2} m

$$1\,D = 10^{-18}\text{ esu cm}$$
$$= 10^{-18} \times (3.335 \times 10^{-10}\,C) \times (10^{-2}\,m)$$
$$= 3.335 \times 10^{-30}\,Cm$$

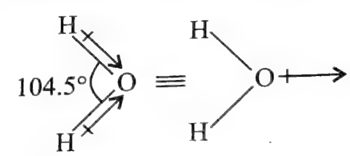
Dipole moment is a vector quantity and is depicted by a small arrow with a tail on the positive centre and head pointing towards the negative centre, e.g. μ of HF is represented as:

$$\overset{+\delta}{H}\longrightarrow\overset{-\delta}{F}$$
$$\longleftrightarrow$$

The shift in electron density is symbolised by crossed arrow ($\leftarrow\!\!\!+\!\!\rightarrow$) above the Lewis structure to indicate the direction of the shift.

2.17.1 BOND MOMENTS

In case of polyatomic molecules, the dipole moments not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. For example, in H_2O molecule, which has a bent structure, the two O – H bonds are oriented at an angle of 104.5°. Net dipole moment of 6.17×10^{-30} C m (1 D = 3.33564×10^{-30} Cm) is the resultant of the dipole moments of two O – H bonds.



(a) Bond dipole (b) Resultant dipole moment

Net dipole moment, μ = 1.85 D

$= 1.85 \times 3.33564 \times 10^{-30}\,Cm = 6.17 \times 10^{-30}\,Cm$

$$\mu_{obs} = 2\mu_{(O-H)} \cos\frac{104.5}{2}$$

$$1.85\,D = 2\mu_{(O-H)} \times 0.613$$

$$\mu_{(O-H)} = 1.51\,D$$

If the individual polar bonds are arranged symmetrically so that the effect of any one bond is cancelled by the effect of the other(s), the net effect or μ will be zero. For example, in $BeCl_2$, individual polar Be—Cl bonds, but the two bond moments are equal and in opposite direction and their vector sum is zero.

$$\underset{\longleftarrow\!+\;\;+\!\longrightarrow}{Cl — Be — Cl}$$

(Net bond moment is zero)

2.18 APPLICATION OF DIPOLE MOMENTS

1. **In determining the polarity of bonds:** As $\mu = q \times d$, obviously, the greater the magnitude of dipole moment, the higher will be the polarity of the bond. But in strict sense, this concept is applicable to molecules containing only one polar bond. Furthermore, in case of non-polar molecules such as H_2, O_2, N_2, etc. the dipole moment is found to be zero. This is because there is no charge separation in these molecules, i.e. $q = 0$. Thus, dipole moment can also be used to distinguish between polar and non-polar molecules.

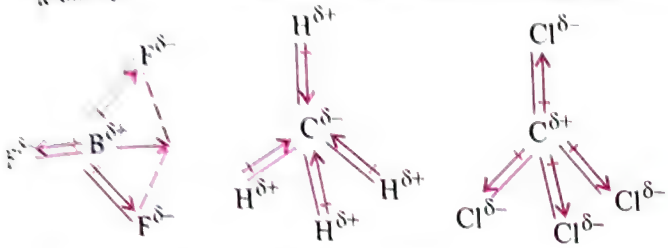


Fig. 2.8 Dipole moment of zero for symmetrical molecules

2. **In calculation of percentage ionic character:** Take example of HCl; its dipole moment is 1.03 D. If HCl was 100% ionic, each end would carry charge equal to one unit viz. 4.8×10^{-10} esu. As bond length of HCl is 1.275 Å, its dipole moment for 100% ionic character would be:

$$\mu_{\text{ionic}} = q \times d = 4.8 \times 10^{-10} \text{ esu} \times 1.275 \times 10^{-8} \text{ cm}$$
$$= 6.12 \times 10^{-18} \text{ esu cm} = 6.12 \text{ D}$$

$$\therefore \% \text{ ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{calculated}}} \times 100$$
$$= \frac{1.03}{6.12} \times 100 = 16.83\%$$

3. **In determining the symmetry (or shape) of molecules:** Dipole moment is an important factor in determining the shape of molecules containing three or more atoms. For instance, if any molecule possesses two or more polar bonds, it will not be symmetrical if it possesses some molecular dipole moment as in case of water (μ = 1.84 D) and ammonia (μ = 1.49 D). But if a molecule contains a number of similar atoms linked to the central atom and the overall dipole moment of the molecule is found to be zero, this will imply that the molecule is symmetrical, e.g. in case of CH_4, CCl_4, etc.

4. **Effect of EN and bond length on dipole moment:** Since the electronegativities (EN) of halogens are more than those of C, so the (C — X) bond is polarised as ($\gtrdot C^{+\delta} - X^{-\delta}$), and hence RX and ArX show dipole moment (μ).

   $\mu = q \times d$ [q = charge, d = distance between the (C — X) bond]

   More the EN of halogen, more is the polarisation of the (C — X) bond and thus greater are the charges on ($C^{+\delta} — X^{-\delta}$). EN of halogens: F > Cl > Br > I.

   As the size of halogens increases, the bond (C — X) increases.

   The order of bond length of (C — X) bond:

   (C — I) > (C — Br) > (C — Cl) > (C — F).

   μ_{observed} : (H_3C — Cl) > (H_3C — F) > (H_3C — Br) > (H_3C — I)

   μ of (H_3C — Cl) is higher than that of (H_3C — F), due to the combined effect of charge and bond length. EN difference between F and Cl is small, therefore, μ of (H_3C — Cl) is higher than that of (H_3C — F). It explains that the bond length of the (C — Cl) bond is more predominant than charge factor.

   EN difference between F and Br or I is much more than the bond length difference in them. Therefore, in (C — Br) and (C — I), the charge factor is more predominant than bond length factor.

Table 2.4 EN of X, (C — X) bond lengths, bond enthalpies and dipole moments

	Bond	EN*	Bond length (pm)	Bond enthalpies ($kJ\ mol^{-1}$)	μ (Debye)
1.	H_3C — F	F = 4	139	452	1.82
2.	H_3C — Cl	Cl = 3.2	178	351	$\boxed{1.94}$
3.	H_3C — Br	Br = 3.0	193	293	1.79
4.	H_3C — I	I = 2.7	214	234	1.64

* EN values are measured by Pauling scale.

5. **Calculation of resultant bond moments:** Let XY and XZ are two polar bonds inclined at an angle θ; their dipole moments are μ_1 and μ_2 (Fig. 2.9).

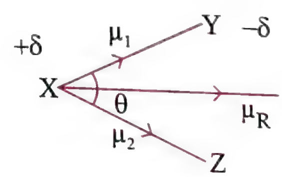
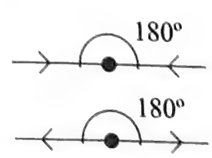


Fig. 2.9

$$\therefore \mu_R = \left(\mu_1^2 + \mu_2^2 + 2\mu_1\,\mu_2 \cos\theta\right)^{\frac{1}{2}}$$

When $\theta = 0°$, μ_R (resultant dipole moment) is maximum.
$\mu_R = \mu_1 + \mu_2$
When $\theta = 180°$, μ_R is minimum.
$\mu_R = \mu_1 - \mu_2$

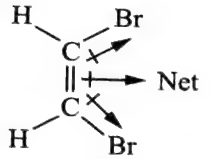


6. **Zero dipole moment:** A molecule having two or more polar bonds may have zero net μ when the molecule has regular structure as expected from hybridisation and centre of action of +ve and –ve poles concides, e.g.

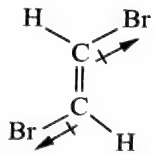
CCl_4	sp^3	109° 28'	Zero μ
PCl_5	sp^3d	120° and 90°	
SF_6	sp^3d^2	90°	
IF_7	sp^3d^3	72° and 90°	

7. Distinguish between cis and trans isomers: Dipole moment can distinguish between geometrical isomers. Generally *cis* isomer has higher μ than *trans* isomer, e.g.,

a. *cis* and *trans* isomers of 1,2 - dibromo ethene.

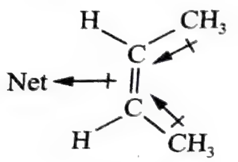


cis (μ ≠ 0)

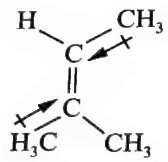


trans (μ = 0)

b. *cis* and *trans* isomers of but -2-ene

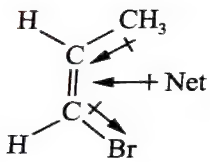


cis (μ ≠ 0)

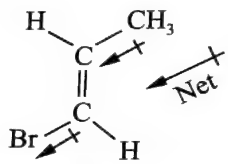


trans (μ = 0)

c. But if groups are different, then μ of *cis* and *trans* may vary, e.g. 1-bromo propene.



(*cis*)



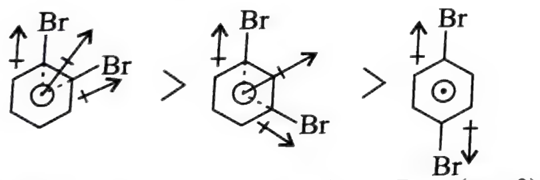
(*trans*)

Net resultant of *trans* isomer is greater than *cis* isomer.

∴ μ (*trans* > μ (*cis*)).

8. Distinguish between o, m and p-isomers:

μ of o- > m- > p-forms



ortho (μ ≠ 0) Meta (μ ≠ 0) Para (μ = 0)

Table 2.5 Dipole moments of selected molecules

Type of molecule	Example	Dipole moment, μ (D)	Geometry
Molecule (AB)	HF	1.78	linear
	HCl	1.07	linear
	HBr	0.79	linear
	HI	0.38	linear
	H_2	0	linear
Molecule (AB_2)	H_2O	1.85	bent
	H_2S	0.95	bent
	CO_2	0	linear
Molecule (AB_3)	NH_3	1.47	trigonal–pyramidal
	NF_3	0.23	trigonal–pyramidal
	BF_3	0	trigonal–planar
Molecule (AB_4)	CH_4	0	tetrahedral
	$CHCl_3$	0	tetrahedral
	CCl_4	0	tetrahedral

ILLUSTRATION 2.15

a. μ of $NH_3 > NF_3$

b. μ of $CH_3Cl > CH_3F > CH_3Br > CH_3I$

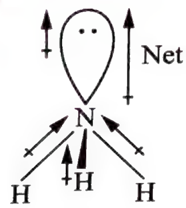
c. μ of CO_2 is zero but μ of $SO_2 \neq 0$

d. Why the lone pair of e^-'s has no effect on the μ of PH_3. The bond angle in PH_3 is 92°.

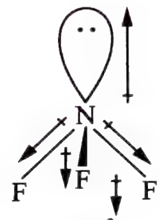
e. μ of $CH_2Cl_2 > CHCl_3$

Sol.

a.



(sp^3)
(a)



(sp^3)
(b)

[Resultant – (μ) of NH_3 = 4.90×10^{-3} Cm   Resultant – (μ) of NF_3 = 0.80×10^{-30} Cm]

In NH_3, the net moment of (N — H) bonds and the contribution from the *lp* e⁻'s (lone pair e⁻'s) are in the same direction and are additive [see figure (a) given above]. The net moment of the (N — F) bond opposes the dipole effect of the *lp* e⁻'s in NH_3 and the resultant is less than μ So, μ of $NH_3 > NF_3$.

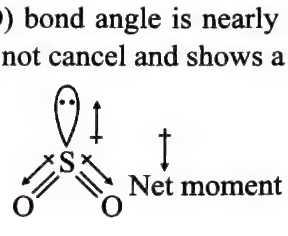
b. The electronegatives of halogens decrease from F to I, So μ of HF > HCl > HBr > HI. But μ of CH_3F is smaller than CH_3Cl due to shorter (C — F) bond distance, although EN of F is greater than that of Cl.

Bond distance factor in CH_3Cl overpowers the charge factor in CH_3F.

c. In CO_2, C is *sp* hybridised and linear. The bond moments of (C — O) are equal and in opposite directions and cancel each other. Hence, μ is zero.

:Ö = C = Ö:

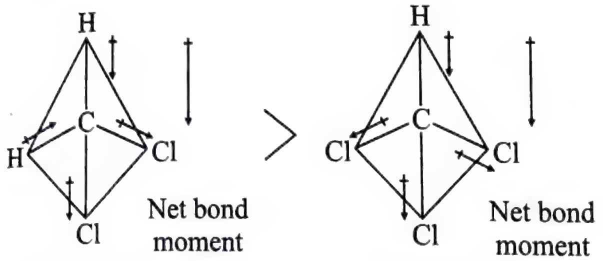
In SO_2, S is sp^2 hybridised having one *lp* e^- on S atom. The (O — S — O) bond angle is nearly 120°; (S — O) bond moment does not cancel and shows a net resultant μ.



d. The 92° bond angle suggests that P uses three p atomic orbitals in forming bonds with H, with one lp e^- in $3s$ atomic orbital, i.e. P in PH_3 is sp^2 hybridised (unlike NH_3, in which N is sp^3 hybridised).

Therefore, due to the presence of lp e^-'s in $3s$ atomic orbital of P, which is spherical symmetrical, the polarity of the molecule is not affected. In order to affect the polarity of the molecule, the e^-'s must be in a directional orbital. Moreover, EN of P and H are nearly same, so PH_3 molecule is almost non-polar.

e.



CH_2Cl_2 (I) > $CHCl_3$ (II)

In (I), all bond moments are in the same direction, so they are additive and the net resultant μ is more than (II).

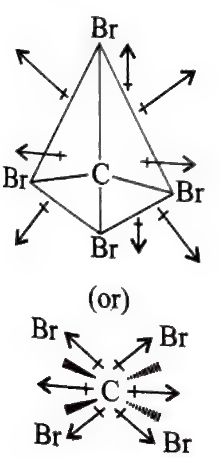
In (II), the bond moment of one of the Cl atoms opposes, the net moment of the other two, so the net resultant μ is less than that of (I).

ILLUSTRATION 2.16

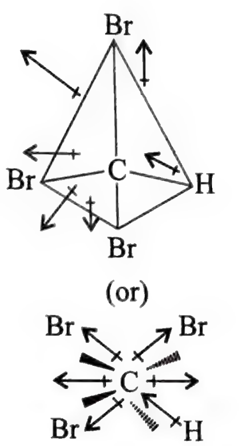
Arrange the following compounds in decreasing order of dipole moment values. Explain the order.

a. CBr_4 b. $CHBr_3$
c. CH_2Br_2 d. CH_3Br

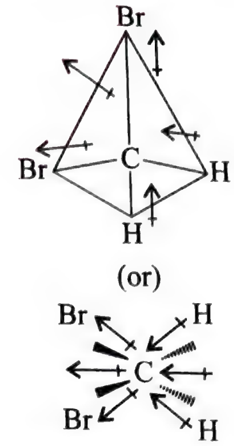
Sol. The three-dimensional structures of three compounds along with the direction of dipole moments in each of their bonds are shown as below:



Net moment = 0
(I) (CBr_4)



Net moment (⟷)
(II) ($CHBr_3$)



Net moment (⟷)
(III) (CH_2Br_2)

a. CBr_4 is symmetrical and therefore has $\mu = 0$.

b. $CHBr_3$, the resultant of two (C—Br) dipoles, is opposed by the resultant of (C—H) and (C—Br) bonds, which is smaller than the former. Therefore, ($CHBr_3$) shows $\mu = 1.01$ D.

c. CH_2Br_2, the resultant of two (C—Br) dipole moments, is reinforced by two (C—H) bonds; therefore, (CH_2Br_2) shows $\mu = 1.52$, which is higher than that of $CHBr_3$.

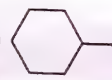
d. (CH_3—Br), due to –I effect of Br, has the highest μ.

Therefore, the order of (μ) is (IV) > (III) > (II) > (I).

ILLUSTRATION 2.17

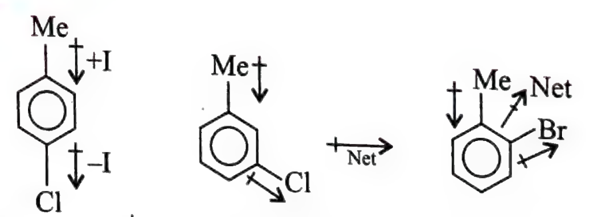
a. Assign orientation to the three chlorotoluenes with $\mu = 1.3$, 1.78, and 1.9 D.

b. Assign orientation to the three cholornitrobenzenes with $\mu = 2.5$, 3.4 and 4.3 D.

c. Which has higher μ: (I) —Br or (II) PhBr?

Sol.

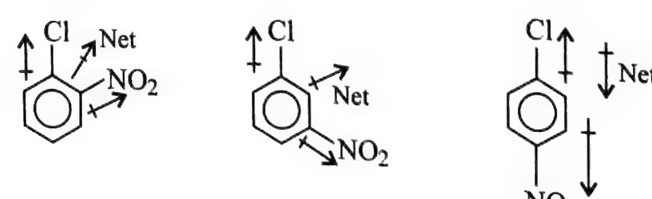
a.



Net moment $\mu = 1.9$ D Net moment $\mu = 1.78$ D Net moment $\mu = 1.3$

μ order = $p > m > o$

b.

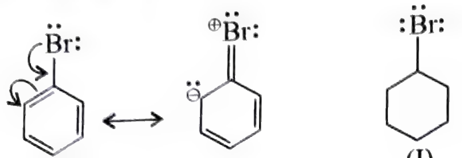


$\theta = 60°$ Net moment ⟶ $\mu = 4.3$ D $\theta = 120°$ Net moment ⟶ $\mu = 3.4$ $\theta = 180°$ Net moment $\mu = 2.5$ D

μ order = $o > m > p$

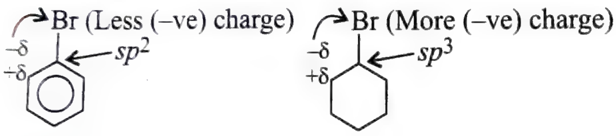
c. μ of (I) > (II)

i. Bromobenzene (II) is resonance stabilised due to delocalisation of *lp* e^-'s of the Br atom in the benzene ring. The (C — Br) bond acquires some double bond character, while in (I) is a single bond, since it does not undergo resonance. In other words, the (C — Br) bond in (II) is shorter than that in (I).



(II) Bromobenzene; (C — Br) has some double bond character; (I) Cyclohexyl chloride (No resonance)

ii. Due to more *s*-character, sp^2-hybridised C is more EN than sp^3-hybrid C atom; therefore, the sp^2-hybrid C of the (C—Br) bond in (II) has less tendency to release e^-'s to Br than an sp^3-hybridised C atom of (I). As a result, the (C—Br) bond in (I) is more polar than in (II), i.e. the magnitude of negative charge (δ^-) is more on Br atom of (I) than in (II).



(II) (I)

Therefore, μ of (I) > (II) [since $\mu = q \times d$ (charge × distance)].

ILLUSTRATION 2.18

Explain the following:

Dipole moment of CH_3F is 1.85 D and that of CD_3F is 1.86 D.

Sol. It is due to the large size of CD_3F, but D is less EN than H ($\mu = q \times d$).

ILLUSTRATION 2.19

a. The dipole moment of HBr is 2.6×10^{-30} Cm and interatomic spacing is 1.41 Å. What is the percent ionic character of HBr?

b. A diatomic molecule has $\mu = 1.2$ D. Its bond distance is 1.0 Å. What fraction of electronic charge exists on each atom?

c. In water, (H—O—H) bond angle is 105°. The distance between (O—H) is 0.94 Å. μ of H_2O = 1.85 D. Determine the magnitude of the charge on the oxygen atom in water molecule and hydrogen atom.

d. BI_3 is a symmetrical planar molecule, all the (B—I) bonds lie at 120° of each other. The distance between the I atoms is 3.54 Å. The radius of covalently bonded I atom is 1.33 Å. Estimate the covalent radius of boron.

e. Calculate the dipole moment of the following compound:

Given: $\mu_{C-Cl} = 1.55$ D

$\mu_{C-NO_2} = 3.95$ D

Sol.

a. Per cent ionic character $= \dfrac{\mu_O}{\mu_C} \times 100$

$$= \frac{2.6 \times 10^{-30}\,\text{Cm}}{1.6 \times 10^{-19}\,\text{C} \times 1.14 \times 10^{-10}\,\text{m}} \times 100 = 11.5\%$$

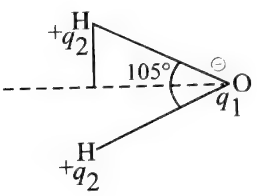
b. $q = \dfrac{\mu}{d} = \dfrac{1.2\ \text{D}}{1.0 \times 10^{-8}\,\text{cm}} = \dfrac{1.2 \times 10^{-18}\ \text{esu cm}}{1.0 \times 10^{-8}\,\text{cm}}$

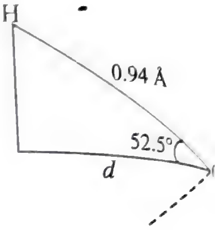
$$= 1.2 \times 10^{-10}\ \text{esu}$$

The fraction of an electronic charge

$$= \frac{1.2 \times 10^{-10}\,\text{esu}}{4.8 \times 10^{-10}\,\text{esu}\ e^{-1}} = 0.25\ e^- = 25\% \text{ of } e^-$$

c. $\mu = 1.85\ \text{D} = 1.85 \times 10^{-18}\ \text{esu cm} = q \times d$





$$\cos 52.5° = \frac{d}{0.94\ \text{Å}} \Rightarrow d = 0.609 \times 0.94\ \text{Å}$$

$$= 0.572\text{Å}$$

$\therefore \mu = q \times d$

$$q_1 = \frac{\mu}{d} = \frac{1.85\ \text{D}}{0.572\ \text{Å}}$$

$$= \frac{1.85 \times 10^{-18}\ \text{esu cm}}{0.572 \times 10^{-8}\ \text{cm}}$$

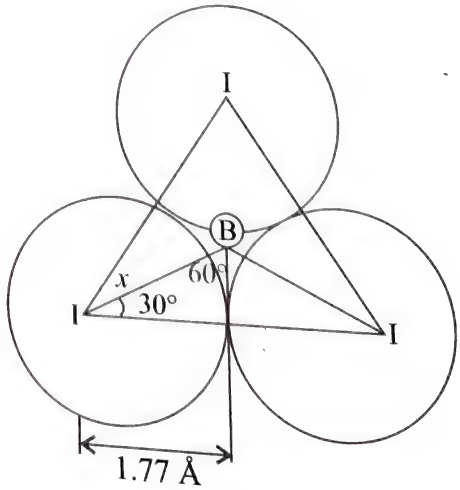
$$= 3.2 \times 10^{-10}\ \text{esu}$$

$q_1 = 2q_2$

$$\therefore\ q_2 = \frac{q_1}{2} = \frac{3.2 \times 10^{-10}}{2}$$

$$= 1.6 \times 10^{-10}\ \text{esu}$$

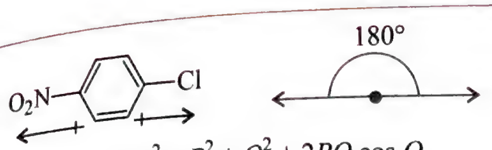
d.



$x = d_{IB}$

$$= \frac{1.77}{\sin 60°} = 2.04\ \text{Å}$$

$r_B = (2.04\ \text{Å}$

e. 

$$R^2 = P^2 + Q^2 + 2PQ \cos Q$$
$$= P^2 + Q^2 + 2PQ \cos 180$$
$$= P^2 + Q^2 - 2PQ$$
$$R^2 = (P - Q)^2$$
$$R = (P - Q)$$
$$\therefore \quad R = 3.95 - 1.55 = 2.4 \text{ D}$$

2.19 THE VALENCE SHELL ELECTRON PAIR REPULSION THEORY

Lewis concept does not explain the shape of molecules but the valence shell electron pair repulsion (VSEPR) theory predicts the shapes of covalent molecules. Sidgwick and Powell in 1940 proposed a simple theory based on repulsive interactions of the electron pairs in the valence shell of the atom. It was further developed and redefined by Nyholm and Gillespie (1957).

The basic concept of VSEPR theory is given as:

1. The central atom is linked to other atoms by covalent bonds by sharing of electrons and there may be some lone pairs (*lp*) of electrons present on central atom. The *lp* of electrons does not take part in the formation of bonds.
2. If the shared pairs on the central atoms are nearer, they will repel each other, which increases the energy of the molecule, thereby decreases the stability of the molecule.
3. If the shared pairs on the central atom are far away, The repulsions between them will be less which decreases the energy of the molecule, thereby increases the stability of the molecule.

   After repulsion between them, the shared pairs take up defined positions around the central atom, hence the molecule adopts a definite shape or geometry.

2.19.1 Main Postulates of VSEPR Theory

The main postulates of VSEPR theory are as follows:

1. The shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom.
2. Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
3. These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
4. The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
5. A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
6. Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.
7. The repulsive interaction of electron pairs decrease in the order:

   Lone pair (*lp*) – Lone pair (*lp*) > Lone pair (*lp*) – Bond pair (*bp*) > Bond pair (*bp*) – Bond pair (*bp*)

2.19.2 Refined VSEPR Model by Nyholm and Gillespie

Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons.

1. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons.
2. This results in greater repulsion between *lp* of electrons as compared to the *lp*–*bp* and *bp*–*bp* repulsions. These repulsion effects result in deviations from idealised shapes and changes in bond angles in molecules.

   Molecules are divided in two categories for the prediction of geometrical shapes of the molecules:

   a. Molecules in which the central atom has no lone pair.

   b. Molecules in which the central atom has one or more lone pairs.

Table 2.6 shows the arrangement of electron pairs about a central atom A (without any lone pairs) and geometries of some molecules/ions of the type AB.

Table 2.7 shows shapes of some simple molecules and ions in which the central atom has one or more lone pairs

Table 2.8 explains the reasons for the distortions in the geometry of the molecule.

In the compounds of AB_2, AB_3, AB_4, AB_5 and AB_6, the arrangement of electron pairs and the B atoms around the central atom A are **linear, trigonal planar, tetrahedral, trigonal bipyramidal and octahedral,** respectively (Table 2.6).

For Example, $BeCl_2$ (AB_2), BF_3 (AB_3), CH_4 (AB_4) and PCl_5 (AB_5) are shown in Fig. 2.10.

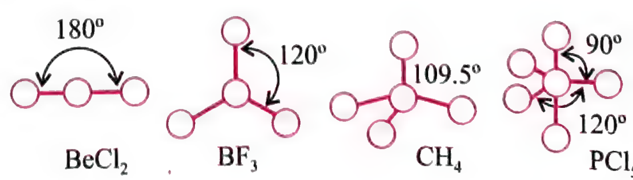
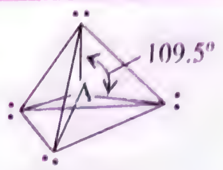
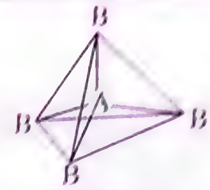
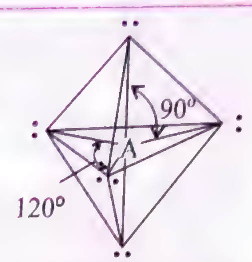
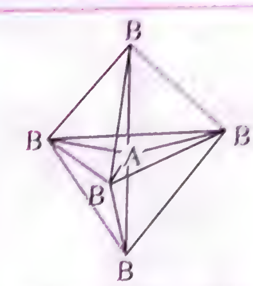
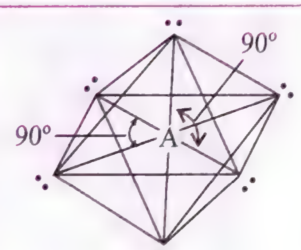
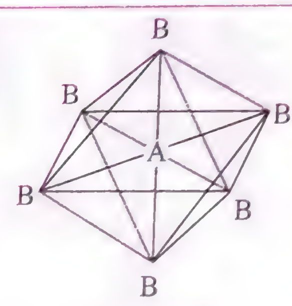


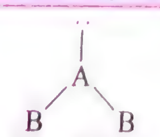
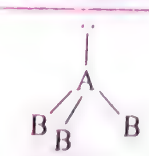
Fig. 2.10 The shapes of molecules in which central atoms has no lone pair

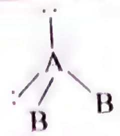
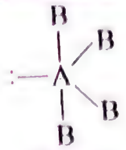
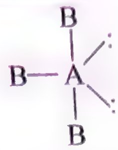
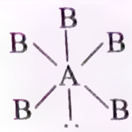
Table 2.6 Geometry of molecules in which the central atom has no lone pair of electrons

S. No.	Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
1.	2	 Linear	B A B Linear	$BeCl_2$, $HgCl_2$
2.	3	 Trigonal planar	 Trigonal planar	BF_3
3.	4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+
4.	5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
5.	6	 Octahedral	 Octahedral	SF_6

Note: A represents central atom/ion. B represents atom(s) attached to central atom of covalent bond. E represents the lp of electrons present on central atom/ion.

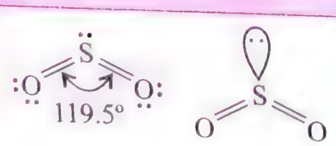
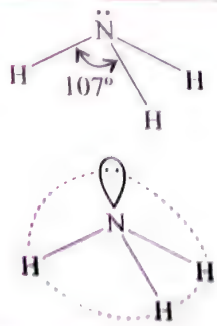
Table 2.7 Shape (geometry) of some simple molecules/ions with central ions having one or more *lp* of e^-'s (E)

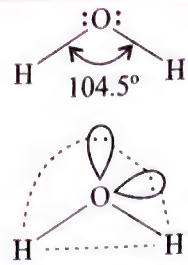
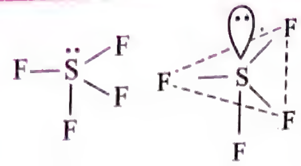
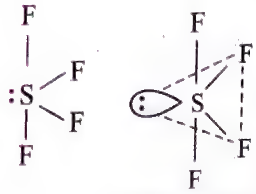
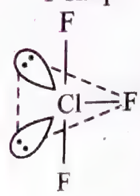
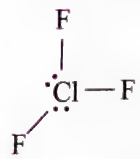
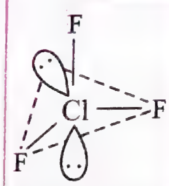
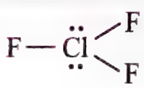
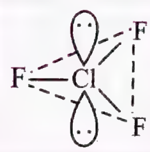
S. No.	Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
1.	AB_2E	2	1	 Trigonal planar	Bent	SO_2, O_3
2.	AB_3E	3	1	 Tetrahedral	Trigonal pyramidal	NH_3

3.	AB_2E_2	2	2	 Tetrahedral	Bent	H_2O
4.	AB_4E	4	1	 Trigonal bipyramidal	See-saw	SF_4
5.	AB_3E_2	3	2	 Trigonal bipyramidal	T-shape or Arrow shape	$Cl\,F_3$
6.	AB_5E	5	1	 Octahedral	Square pyramid	BrF_5
7.	AB_4E_2	4	2	 Octahedral	Square planer	XeF_4

Note: A represents central atom/ion. B represents atom(s) attached to central atom of covalent bond. E represents the lp of electrons present on central atom/ion.

Table 2.8 Shapes of molecules containing bond pair and lone pair

S. No.	Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason of the shape acquired
1.	AB_2E	2	1		Bent	Theoretically the shape should have been triangular planar but actually it is found to be bent or V-shaped. The reason being the *lp–bp* repulsion is much more as compared to the *bp–bp* repulsion. So, the angle is reduced to 119.5° from 120°.
2.	AB_3E	3	1		Trigonal pyramidal	Had there been a *bp* in place of *lp* the shape would have been tetrahedral but one lone pair is present and due to the repulsion between *lp* and *bp* (which is more than *bp* and *bp* repulsion) the angle between bond pairs is reduced to 107° from 109.5°.

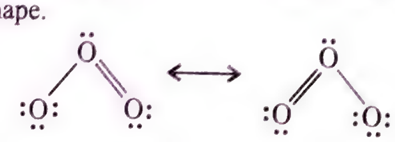
3.	AB_2E_2	2	2		Bent	The shape should have been tetrahedral if there were all *bp* but two *lp* are present so the shape is distorted tetrahedral or angular. The reason is *lp–lp* repulsion is more than *lp–bp* repulsion which is more than *bp–bp* repulsion. Thus, the angle is reduced to 104.5° from 109.5°.
4.	AB_4E	4	1	a.  b.  (More stable)	See-saw or folded square or distorted tetrahedral	In (a), the *lp* is present at axial position so there are three *lp–bp* repulsions at 90°. In (b), the *lp* is on equatorial position, and there are two *lp–bp* repulsions. Hence, arrangement (b) is more stable. The shape shown in (b) is described as a distorted tetrahedron, a folded square or a see-saw.
5.	AB_3E_2	3	2	a. 	T-shape 	In (a) the *lp* are at equatorial position so there are less *lp–bp* repulsions as compared to others in which the *lp* are at axial positions. So, structure (a) is most stable (T-shaped).
				b. 		
				c. 		

Note: A represents central atom/ion. B represents atom(s) attached to central atom of covalent bond. E represents the lp of electrons present on central atom/ion.

Note: In predicting geometry of molecules containing double bond, the double bond is considered as one electron pair. For example, in case of ozone, its two resonating structures are

$$:\ddot{O}-\ddot{O}=\ddot{O} \longleftrightarrow \ddot{O}=\ddot{O}-\ddot{O}:$$

In each structure, the central atom has one lone pair and two bond pairs (counting double bond as one bond pair). Hence, it has a bent shape.



2.19.3 Applications of VSEPR Theory

1. The VSEPR theory is able to predict geometry of a large number of molecules, especially the compounds of p-block elements accurately.
2. It is also quite successful in determining the geometry quite accurately even when the energy difference between possible structures is very small.

2.19.4 Limitations of VSEPR Theory

1. It had limited application because it is unable to predict the shape in a number of cases.
2. Effect of electron pair repulsion on molecular shape is not very clear.
3. Direction of electron pairs does not seem to very rational.

2.20 VALENCE BOND THEORY

Lewis approach helps in writing the structure of molecules, but it fails to explain the formation of chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies

and bond lengths in molecules such as H_2 (435.8 kJ mol^{-1}, 74 pm) and F_2 (150.6 kJ mol^{-1}, 42 pm), although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. It also gives no idea about the shapes of polyatomic molecules.

Similarly, the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also it has limited applications. To overcome these limitations, the two important theories based on quantum mechanical principles are introduced. These are valence bond theory (VBT) and molecular orbital theory (MOT).

Valence bond theory was introduced by Heitler and London (1927) and developed further by Pauling and Slater.

VBT is based on the following information:

1. Electronic configuration of elements.
2. Knowledge of atomic orbitals.
3. Overlap of atomic orbitals.
4. Hybridisation of atomic orbitals.
5. Principles of variation and superposition.

2.20.1 VBT in Terms of Energy Consideration

When two atoms are far apart from each other, there is no interaction between them. When they come closer to each other, the new forces come into operation. These forces are of two types:

1. *The forces of repulsion between the nuclei of these combining atoms and between the electrons of these atoms.* These forces tend to increase the energy of the system.
2. *The forces of attraction between the nucleus of one atom and electrons of the other atom.* These forces tend to decrease the energy of the system.

   If in a system, these new forces can decrease the energy, then possibility of chemical bonding exists and if these forces lead to increase in energy, the chemical bonding is not possible.

2.20.2 Formation of H_2 Molecule

Consider two hydrogen atoms A and B approaching each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B. When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.

Attractive forces arise between (i) nucleus of one atom and its own electron, i.e. $N_A - e_A$ and $N_B - e_B$ and (ii) nucleus of one atom and electron of other atom i.e., $N_A - e_B$, $N_B - e_A$.

Similarly, repulsive forces arise between (i) electrons of two atoms like $e_A - e_B$, and (ii) nuclei of two atoms $N_A - N_B$.

Attractive forces bring the two atoms close to each other whereas repulsive forces push them apart. (Fig. 2.11)

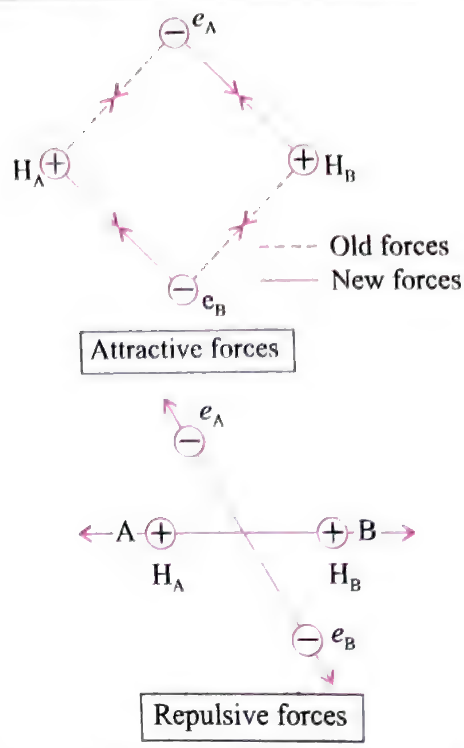


Fig. 2.11 Forces of attraction and repulsion during the formation of H_2 molecule

The magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Ultimately a stage is reached where the net force of attraction equals the force of repulsion and the system acquires minimum energy. At this stage, two hydrogen atoms are bonded together to form a stable molecule having the bond length of 74 pm.

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as bond enthalpy, which is corresponding to minimum in the curve depicted in Fig. 2.12. Conversely, 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.

$$H_{2(g)} \longrightarrow H_{(g)} + H_{(g)} \qquad \Delta_a H^{\ominus} = 435.8 \text{ kJ mol}^{-1}$$

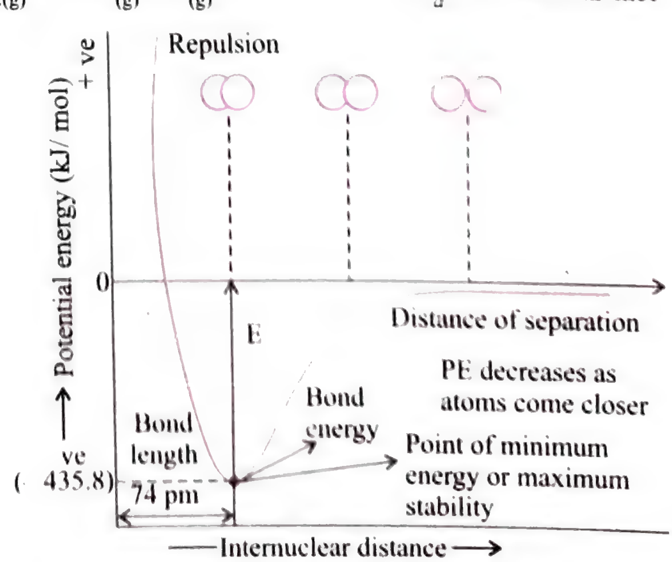


Fig. 2.12 The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2.

2.20.3 Why Helium Molecule (He_2) is not Formed

When the two atoms of He approaches to each other, four new forces of attraction and five new forces of repulsion occurs. The attractive forces are between the two nuclei and the four electrons of the two atoms while out of the repulsive forces, one is between nuclei of the two atoms and the remaining four are among the electrons. As a result of these new interactions, repulsive forces are greater than the attractive forces and so the energy of the system increases. Hence, no chemical bond is possible. [Figs. 2.13(a) and (b)].

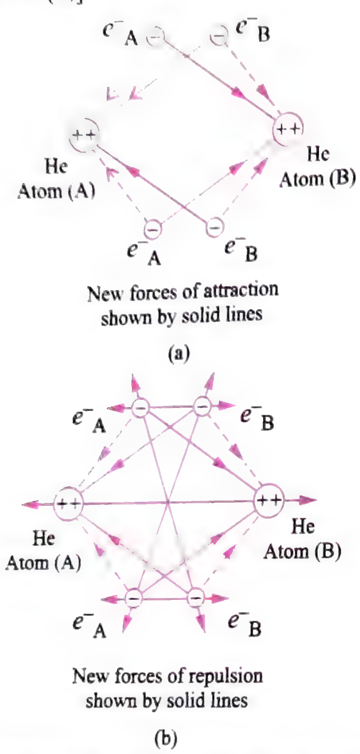


Fig. 2.13. (a and b) New forces of attraction and repulsion in case of two helium atoms approaching each other

Thus, energetically the formation of helium molecule is not possible because there is an increase in the potential energy of the system when two helium atoms approach each other as shown in Fig. 2.14.

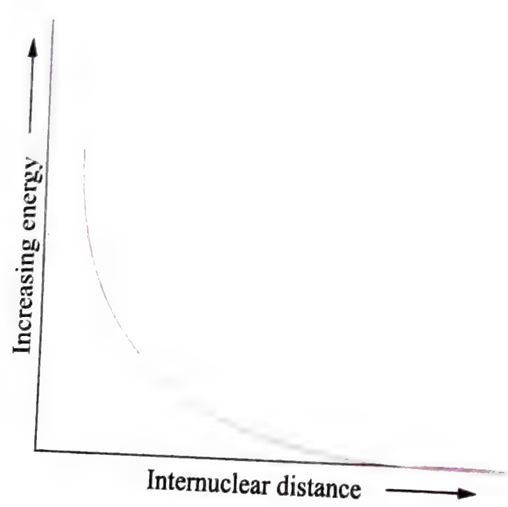


Fig. 2.14. Variation of potential energy when two helium atoms approach to each other

2.20.4 Orbital Overlap Concept of Covalent Bond

According to this concept, a covalent bond is formed by the partial overlap of two half-filled orbitals containing electrons with opposite spins.

The 'partial overlap' means that a part of the electron cloud of each of the two half-filled atomic orbitals becomes common. As a result, the probability of finding the electrons in the region of overlap is much more than at other places. Thus, the two electrons (with opposite spins) although keep on exchanging position between the two atoms but are present for maximum time in the region of overlap and hence are attracted to both the nuclei simultaneously thereby forming a bond between the two atoms.

In fact, after the overlap, the two atomic orbitals merge into each other resulting into the formation of a new orbital called molecular orbital.

To understand the concept more clearly, consider the following examples:

1. **Formation of H_2 molecule:** In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the in the pairing of electrons.
   - **a.** The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms.
   - **b.** Therefore, according to the orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.

   The molecule of H_2 is formed due to overlap of 1*s*-orbitals of two H-atoms (i.e. *s*–*s* overlap), when they combine with each other (Fig. 2.15).

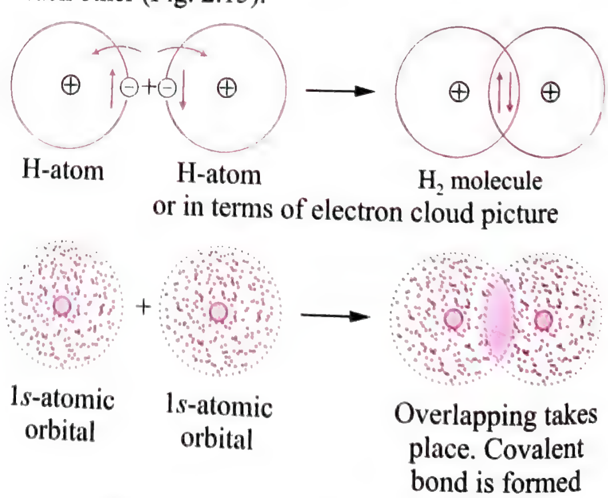


Fig. 2.15 Formation of hydrogen molecule

2. **Formation of hydrogen fluoride molecule:** In case of formation of hydrogen fluoride molecule, when one atom of fluorine (valence electronic configuration. $2s^2\,2p_x^{\,2}\,2p_y^{\,2}\,2p_z^{\,1}$) having one unpaired e^- in its p-orbital comes closer to H-atom with e^-'s of opposite spin in its 1*s*-orbital, then the two half-filled orbitals overlap each other and a chemical bond is formed between the two atoms.

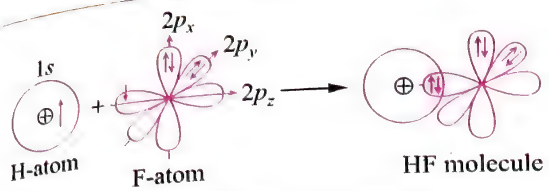
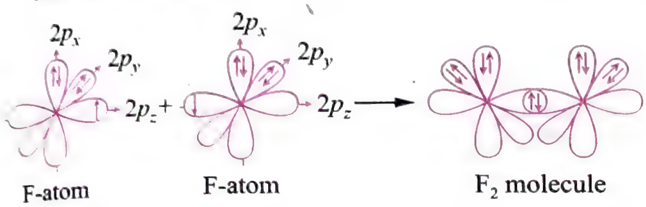


Fig. 2.16 Formation of HF molecule

3. **Formation of fluorine molecule:** When an atom of fluorine (valence electronic configuration: $2s^2\,2p_x^2\,2p_y^2\,2p_z^1$) approaches another atom of fluorine having an electron of opposite spin in $2p_z$ orbital, the half-filled orbitals overlap each other resulting in the formation of a fluorine molecule



Formation of fluorine molecule

2.20.5 Existence of Only H_2 and Non-existence of Species Like H_3 and H_4

This can be easily explained on the basis of orbital concept. A hydrogen atom contains only one half-filled atomic orbital ($1s$) which can overlap with the half-filled atomic orbital of another hydrogen atom, forming H_2. No more half-filled atomic orbital is available and so no more bond can be formed.

Non-formation of He_2: This can also be explained on the basis of orbital concept. A helium atom contains fully-filled atomic orbital ($1s^2$) which cannot overlap with the $1s$ orbital of another helium atom because only half-filled atomic orbitals can overlap with each other. Thus, He_2 is not formed.

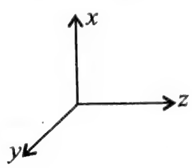
2.20.6 Directional Properties of Covalent Bonds

In case of polyatomic molecules such as CH_4, NH_3 and H_2O, the geometry of the molecules is also important in addition to the bond formation. For example, why is it so that CH_4 molecule has tetrahedral shape and HCH bond angles are 109.5°? Why is the shape of NH_3 molecule pyramidal?

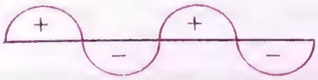
The valence bond theory explains the formation and directional properties of bonds in polyatomic molecules such as CH_4, NH_3 and H_2O etc. in terms of overlap and hybridisation of atomic orbitals.

2.20.7 Overlapping of Atomic Orbitals

When two atoms come close to each other, there is overlapping of atomic orbitals. Using the approrpriate signs for the wave function of atomic orbitals the overlap may be positive, negative or zero depending upon the properties of overlapping of atomic orbitals. The various arrangements of s and p orbitals resulting in positive, negative and zero overlap are shown in Fig. 2.17.



Note: z-axis is chosen as the internuclear axis. Sign ⊕ and ⊖ are not charges but represent the phases of the waves of atomic orbitals as shown.



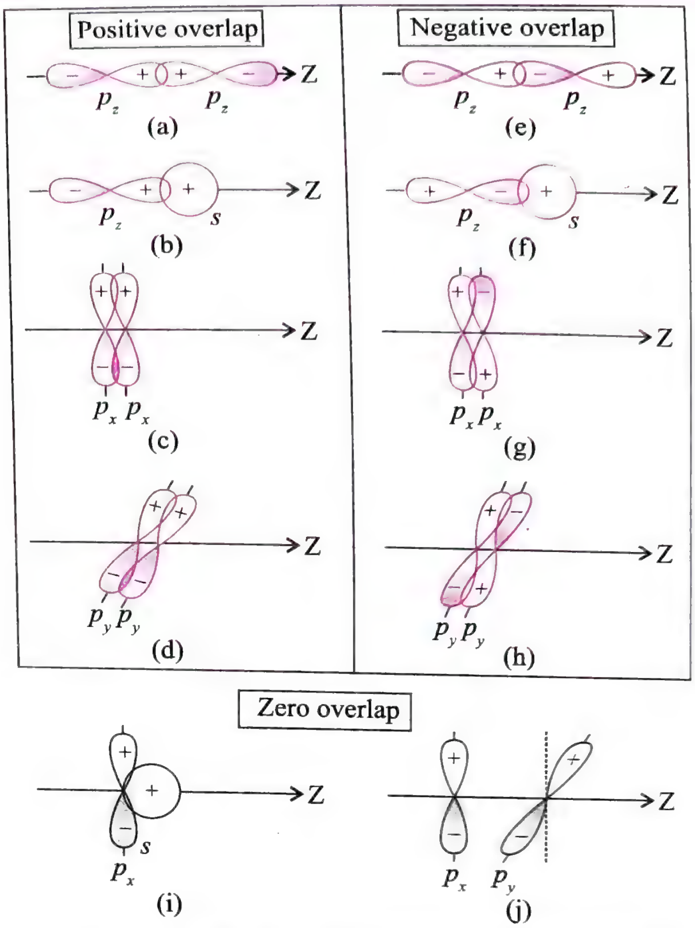


Fig. 2.17 Positive, negative and zero overlaps of s and p atomic orbitals

2.20.8 Main Points of VBT

Two essential conditions for the formation of a chemical bond are as follows:

1. There should be maximum overlapping of the involved atomic orbitals of the two atoms.
2. Each of the two involved atomic orbitals must have one unpaired electron with an opposite spin.

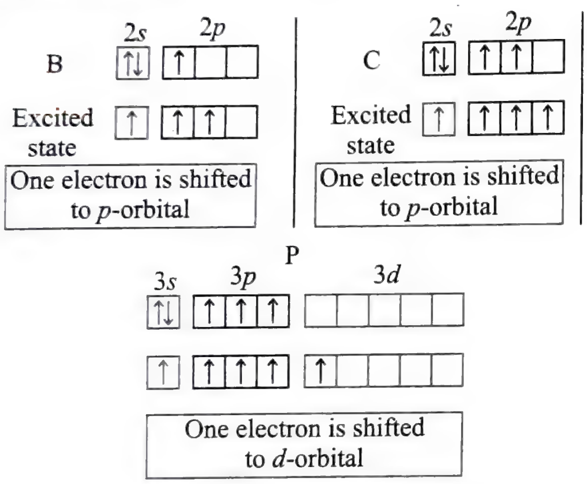
   The orbital concept was presented by Heitler and London, in 1927. This concept is also known as valence bond theory or modern concept of covalent bond. The main points of the theory are as follows:

   a. A covalent bond is formed by overlapping of atomic orbitals of valence shell of the two atoms.
   b. Only half-filled atomic orbitals, i.e. orbitals singly occupied can enter into overlapping process. The resulting bond acquires pair of electrons with opposite spins.
   c. The atoms with half-filled orbitals must come closer to one another with their axes in proper directions for overlapping.

d. As a result of overlapping, there is maximum electron density somewhere between the two atoms. A large part of bonding force comes into existence from the electrostatic attraction between the nuclei and the accumulated electron cloud between them.

e. Greater the overlapping, higher is the strength of the chemical bond. The amount of energy released per mole during overlapping is termed bond energy. This energy stabilises the system. Hence, the molecule formed has less energy and consequently more stability than the isolated atoms.

f. Electrons which are already paired in valence shell can enter into bond formation if they can be unpaired first and shifted to vacant orbitals of slightly higher energy of the same main energy shell (valence shell). This point explains the trivalency of boron, tetravalency of carbon, pentavalency of phosphorous, hexavalency of sulphur and heptavalency of halogens (Cl, Br, 1) inspite of the fact that these atoms have paired orbital or orbitals in the valence shell.



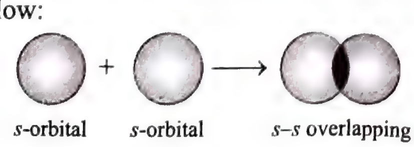
g. Between two orbitals of the same stability (i.e. having same energy) one more directionally concentrated would form a stronger bond. **Dumb-bell-shaped p-orbitals** will form stronger bond as compared to spherical symmetrical *s*-orbitals. It is formed by head on or axial overlap.

2.20.9 Types of Overlapping and Nature of Covalent Bonds

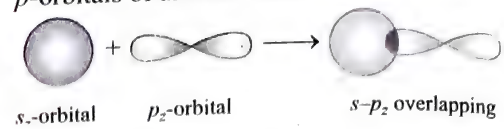
The covalent bond may be classified into two types depending upon the types of overlapping: Sigma (σ) bond and pi (π) bond.

1. **Sigma (σ) bond**: This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

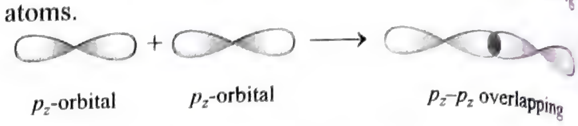
   a. ***s–s* overlapping**: In this case, there is overlap of two half-filled *s*-orbitals along the internuclear axis as shown below:



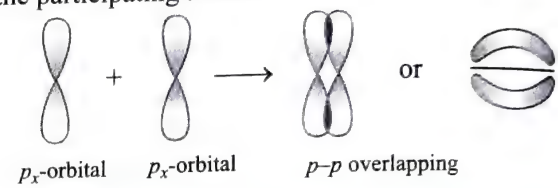
   b. ***s–p* overlapping:** This type of overlap occurs between half-filled *s*-orbitals of one atom and half-filled *p*-orbitals of another atom.



   c. ***p–p* overlapping**: This type of overlap takes place between half-filled *p*-orbitals of the two approaching atoms.



2. ***pi* (π) bond**: In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two **saucer type** charged clouds above and below the plane of the participating atoms.



2.20.10 Strength of Sigma and Pi Bonds

Basically, the strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that pi bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bond (double or triple bonds).

The bond strength order of the following molecules is:

H – F >	H – H >	F – F
(1*s* – 2*p*)	(1*s* – 1*s*)	(2*p* – 2*p*)
Overlap	Overlap	Overlap

Note:

i. *A π bond is never formed alone. It is formed along with a σ bond.*

ii. Whenever there is a multiple bond, i.e. double and triple bonds, π bond is formed.

iii. In π bond, the electron density lies above and below the imaginary line joining the centres of nuclei of bonded atoms.

Table 2.9 Comparison of sigma and pi bond

Sigma bond	Pi bond
1. The bond is formed by the overlap of orbitals along their axes (end to end overlap). It includes *s*–*s*, *s*–p_z and p_z–p_z overlapping.	1. The bond is formed by sidewise overlapping of orbitals (lateral overlapping). It includes *p*–*p* overlapping. ($p_x - p_x$, $p_y - p_y$)
2. Electron cloud is symmetrical about the line joining the two nuclei.	2. Electron cloud is unsymmetrical.

3. It is a strong bond.	3. It is a weak bond.
4. These are less reactive.	4. These are more reactive.
5. The shape of the molecule is determined by these bonds.	5. These bonds do not affect the shape of the molecule.
6. There can be free rotation of atoms around this bond.	6. Free rotation is not possible around this bond.
7. σ-bond can have independent existence.	7. π-bond always exists along with a σ-bond.
8. σ-electrons are referred as localised.	8. π-electrons are referred as mobile electrons.

2.20.11 Examples of Formation of Compounds by Orbital Overlap Concepts and the Failure of Orbital Overlap Concept

The criterion of overlap for the formation of covalent bonds applies uniformly to homonuclear/heteronuclear diatomic and polyatomic molecules.

Shapes of polyatomic molecules such as, CH_4, NH_3 and H_2O are tetrahedral, pyramidal and bent respectively. But simple atomic orbital overlap does not account for the directional characteristics of bonds and bond angles in the molecules such as CH_4, NH_3 and H_2O and other molecules or ions.

1. **Formation of CH_4 molecule:** Valence electronic configuration of C in its ground state = $2s^2\ 2p^2$. Valence electronic configuration of C in its excited state is $2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$.

   The energy required for this excitation is compensated by the release of energy due to overlap between orbitals of C and H atoms.

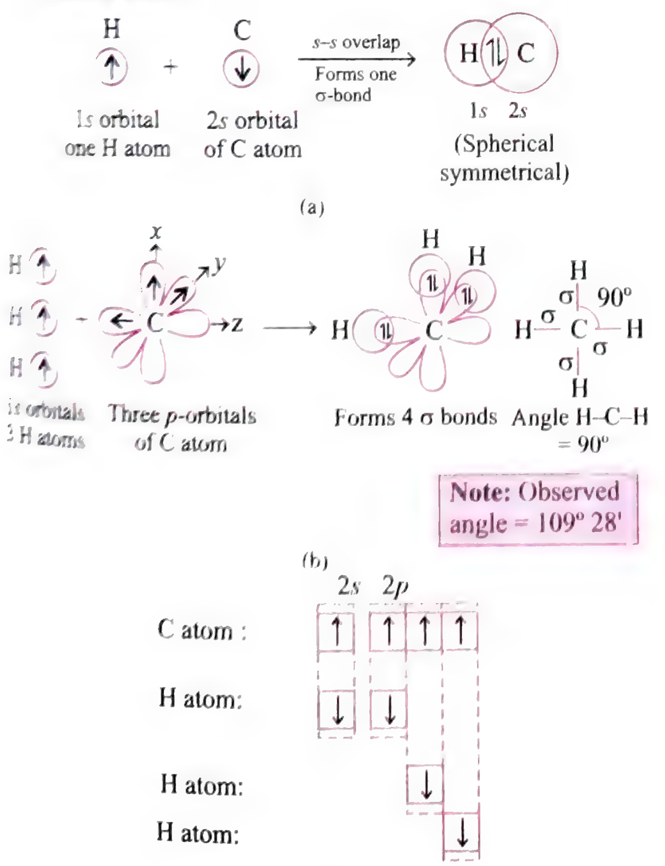


Fig. 2.18 (a and b) Formation of CH_4 molecule by s–p overlapping. (c) Another method of representing the formation of CH_4 molecule

The four atomic orbitals of carbon, each with an unpaired electron can overlap with the 1*s* orbitals of the four H atoms which are also singly occupied. This will result in the formation of four C–H bonds. It was found that while the three *p* orbitals of carbon are at 90° to one another, the HCH angle for these will also be 90°. That is, three C–H bonds will also be oriented at 90° to one another.

The 2*s* orbital of carbon and the 1*s* orbital of H are spherically symmetrical and they can overlap in any direction. Therefore, the direction of the fourth C–H bond cannot be ascertained.

This description does not fit in with the tetrahedral HCH angles of 109.5°. Clearly, it follows that simple atomic orbital overlap does not account for the directional characteristics of bonds in CH_4 [Figs. 2.18(a), (b) and (c)].

2. **Formation of H_2O molecule:** Valence electronic configuration of O atom (Z = 8) is $2s^2\ 2p_z^2\ 2p_x^1\ 2p_y^1$, i.e. it has two orbitals singly occupied. These two orbitals overlap with 1*s*-orbitals of 2H-aotms forming 2σ-bonds.

   Since the two orbitals of O atom are at right angles to each other an angle of 90° is expected between 2σ bonds but the actual bond angle observed is 104.5° [Figs. 2.19(a) and (b)].

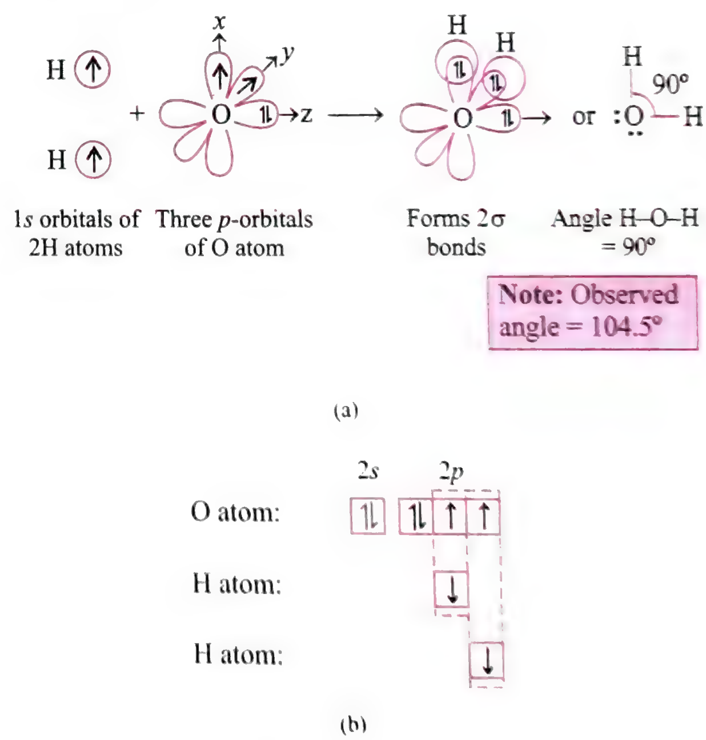


Fig. 2.19 (a) Formation of H_2O molecule by s–p overlapping. (b) Another method of representing the formation of H_2O molecule

3. **Formation of NH_3 molecules:** Valence electronic configuration of N atom (Z = 7) is $2s^2$, $2p_z^1\ 2p_x^1\ 2p_y^1$, i.e. it has three singly occupied orbitals. These orbitals overlap with 1*s*-orbitals of 3H-atoms forming 3σ-bonds.

   Since the three orbitals of N atom are at right angles to each other, the expected angle between H – N – H (i.e. between 2σ-bonds) should be 90° but observed bond angle is 107° [Figs. 2.20(a) and (b)].

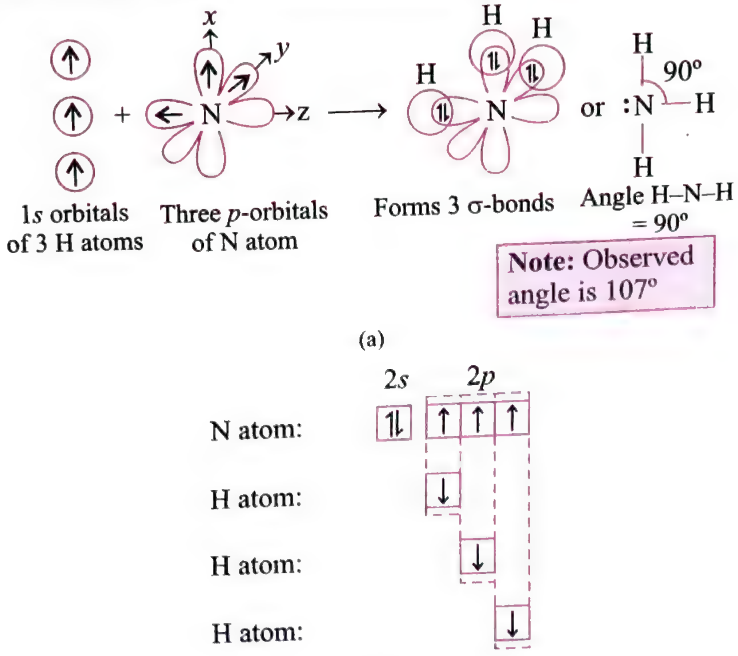


Fig. 2.20 (a) Formation of NH_3 molecule by s–p overlapping. (b) Another method of representing the formation of NH_3 molecule

ILLUSTRATION 2.20

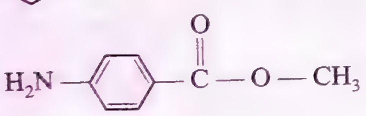
Calculate the number of σ, π and non-bonding (i.e. lone pair) electrons in the following compounds.

a. $H_2C = CH - CH = CH_2$

b. $H_3C - C \equiv C - CH = CH - CH_3$

c.

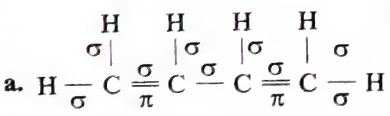
d.



e. $H_3C - \underset{\underset{CH_3}{|}}{CH} - \overset{\overset{O}{\|}}{C} - C \equiv C - CH = CH - C \equiv N$

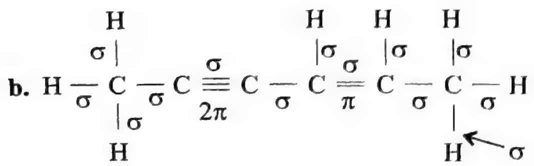
Sol.

a.



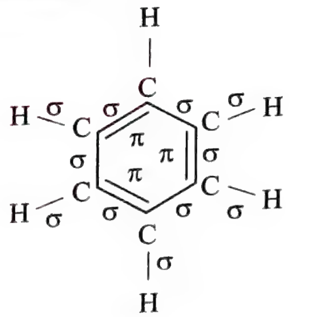
[No. of σ-bonds = 9
No. of π-bonds = 2
No. of non-bonding e^-'s = 0]

b.



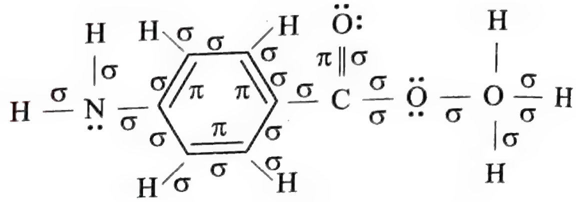
[No. of σ-bonds = 13
No. of π-bonds = 3
No. of non-bonding e^-'s = 0]

c.



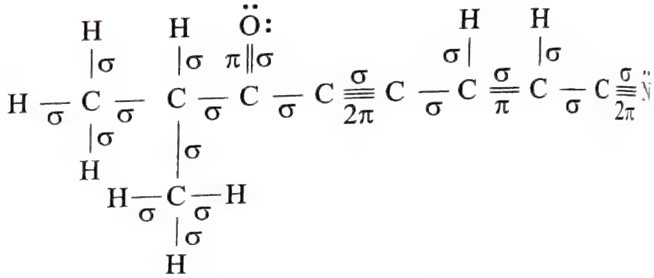
[No. of σ-bonds = 12
No. of π-bonds = 3
No. of non bonding e^-'s = 0]

d.



[No. of σ-bonds = 20
No. of π-bonds = 4
No. of non-bonding e^-'s = 10
No. of lone pairs (*lp*) = 5]

e.



[No. of σ-bonds = 19
No. of π-bonds = 6
No. of non-bonding e^-'s = 6
No. of lone pairs (*lp*) = 3]

2.21 CONCEPT OF HYBRIDISATION

A covalent bond is formed by the overlap of half atomic orbital (i.e. containing one electron). Therefore, the covalency of the element should be equal to the number of half-filled orbitals present in an atom of the element. However, on the basis of VBT, the formation and their properties (e.g. bond characteristics, such as bond length and bond energy) of many compounds such as those of B, Be and C (e.g. BeF_2, BF_3 and CH_4) could not be explained.

Considering the valence electronic configuration of Be, B and C in the ground and excited state are as follows:

Element with atomic number	Valence electronic configuration in ground state	Valence electronic configuration in excited state
Be (Z = 4)	$2s^2\,2p^0$	$2s^1\,2p^1$
B (Z = 5)	$2s^2\,2p_z^{\,1}$	$2s^1\,2p_z^{\,1}\,2p_x^{\,1}$
C (Z = 6)	$2s^2\,2p_x^{\,1}\,2p_y^{\,1}$	$2s^1\,2p_x^{\,1}\,2p_y^{\,1}\,2p_z^{\,1}$

Valence electronic configuration of Be, B and C in ground state shows that they possess 0, 1 and 2 covalenceis respectively. Since Be has no half-filled AO's, B has one and C has two. But actually

it was observed that (i) Be has a covalency of 2 in BeF_2, (ii) B has a covalency of 3 in BF_3 and (iii) C has a covalency of 4 in CH_4, CCl_4, CO_2 etc.

The above problem was solved by considering that under the conditions of bond formation the 2*s*-paired orbital gets unpaired and one electron is promoted to the vacant 2*p* orbital without consuming excessive energy.

For example, consider the formation of CH_4.

	2s	2p
C atom in ground state:	⇅	↑ ↑ □
C atom in excited state:	1	1 1 1

Thus, in the excited state the C has four half-filled orbitals which are available for overlapping and thus forms four bonds with H atoms to form a molecule of CH_4 [as shown in Figs 2.18 (a), (b) and (c)].

From Figs. 2.18(a), (b) and (c), it is clear that three (C–H) bonds are formed by the overlap of three 2*p*-orbitals of C with 1*s*-orbital of each H atom. The fourth (C–H) bond is formed by the overlap of 2*s*-orbital of C with 1 *s*-orbital of H atom. Thus, one bond is different from the other three. But this is not true. The CH_4 molecule possesses the following characteristics:

1. All the four (C–H) bonds are identical as shown experimentally by the formation of only one monochloro methane.

   $CH_4 \xrightarrow{Cl_2,\ h\nu} CH_3Cl$

2. All the four bonds are not present in the same plane. Actually, there is a tetrahedral bond angle, i.e. 109° 28′. Thus, it is observed that all the four (C–H) bonds in CH_4 molecule are of equal bond strength and bond length.

   Hence to have four identical (C–H) bonds, C atom must contribute a set of four equivalent orbitals. This is possible when one 2*s*- and three 2*p*-orbitals of C atom in the excited state mix together to form four equivalent orbitals.

2.21.1 Hybridisation

1. The process of mixing of atomic orbitals belonging to the same atom of slightly different energies so that a redistribution of energy takes place between them resulting in the formation of new set of orbitals of equivalent energies and shape is called *hybridisation*. The new orbitals thus formed are known as hybrid orbitals. Unlike pure orbitals, the hydrid orbitals are used in bond formation.
2. It is a hypothetical concept and has been introduced by Pauling and Slater in order to explain the characterisic geometrical shapes of poly atomic molecules such as CH_4, NH_3 and H_2O.
3. The energy required for excitation of electrons becomes avaliable when the combining atoms approach each other because energy is released when combining atoms approach each other.

Note: That is why hybridisation never takes place in isolated atoms but occurs only at the time of bond formation.

4. The shape of hybrid orbitals (e.g. made from *s*- and *p*-orbitals) is like that of *p*-orbital except that the two lobes are unequal in size, i.e. there is one small lobe (with –ve sign) opposite to a big lobe (with +ve sign) on the other side (Fig. 2.21).

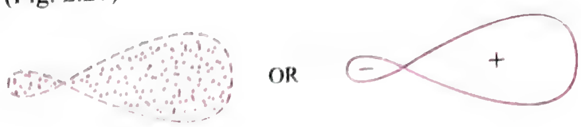


Fig. 2.21 Representation of a hybrid orbital

2.21.2 Salient Features of Hybridisation

The main features of hybridisation are as follows:

1. Only atomic orbitals of nearly same energy belonging to same atom or ion takes part in hybridisation.
2. The number of hybrid orbitals is equal to the number of atomic orbitals that get hybridised.
3. The hybridised orbitals are always equivalent in energy and shape.
4. The electron waves in hybrid orbitals repel each other and thus tends to be farthest apart.
5. Hybrid orbitals form only sigma (σ) bond. π bond is always excluded from hybridisation.
6. The hybrid orbitals are more effective in forming stable bond than the pure atomic orbitals.
7. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

2.21.3 Important Conditions for Hybridisation

1. The orbitals undergoing hybridisation should have almost equal energy.
2. Promotion of electron is not an essential condition prior to hybridisation.
3. It is not necessary that only half-filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.
4. The orbitals present in the valence shell of the atom are hybridised, i.e. it is the orbitals and not the electrons that undergon hybridisation. For example, four orbitals of N atom ($2s^2\,2p_x^{\,1}\,2p_y^{\,1}\,2p_z^{\,1}$) belonging to valence shell when hybridise, form 4-hybrid orbitals, one of which contains two electrons (as before) and other three have one electron each.
5. The molecule has a *regular geometry* if all the hybrid orbitals after overlapping contain shared pair of electrons (i.e. bonding electrons).
6. If, however, the central atom is surrounded by one or more orbitals containing lone pairs (*lp*) of electrons in the valence shell, the geometry of the molecule is *distored* to some extent. The bond angle is also affected to some extent, due to repulsion between *lp*'s with *bp*'s. Such observation has been found, for example, in the NH_3 and H_2O molecules.

2.21.4 Types of Hybridisation

The different types of hybridisation are as follows:

1. **Diagonal or linear or *sp* hybridisation:** When one *s*- and one *p*-orbital belonging to the same main shell of an atom are mixed together to form two new equivalent orbitals, the type of hybridisation is called *sp* hybridisation or diagonal hybridisation. The new orbitals formed are called *sp* hybrid orbitals.

   They are collinear with an angle of 180° as shown in Fig. 2.22.

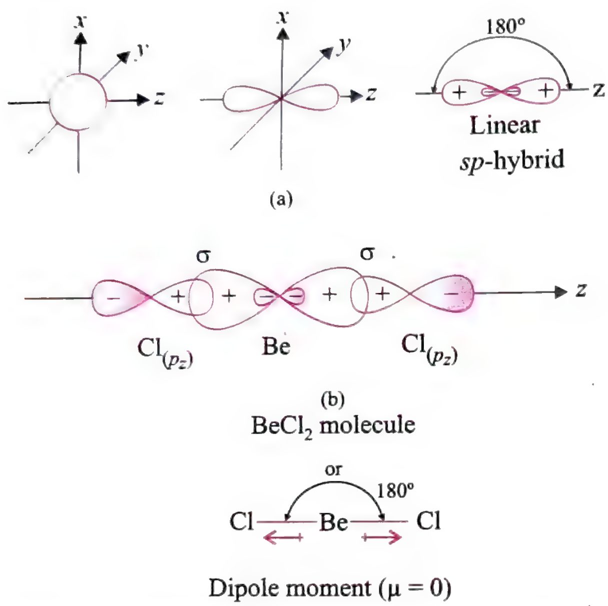


Fig. 2.22 (a) Formation of sp hybrids from s- and p-orbitals. (b) Formation of the linear $BeCl_2$ molecule.

Each of the hybrid orbitals formed has 50% *s* character and 50% *p* character. The remaining two *p*-orbitals which do not participate in the hybridisation remain as such. If these are half-filled, they may form bonds with other atoms having half-filled atomic orbitals. For example,

a. BeF_2, BeH_2, etc.

b. All compounds of carbon containing triple bond ($C \equiv C$) such as acetylene (C_2H_2) and in cumulated dienes, e.g. $H_2C = \underset{\uparrow \atop sp}{C} = CH_2$, are sp hybridised.

2. **Trigonal planar or sp^2 hybridisation:** When one *s*- and two *p*-orbitals of the same shell of an atom mix to form three new equivalent orbitals, the type of hybridisation is called sp^2 hybridisation or trigonal hybridisation. The new orbitals formed are called sp^2 hybrid orbitals.

   All the three hybrid orbitals remain in the same plane making an angle of 120° with one another as represented in Fig. 2.23.

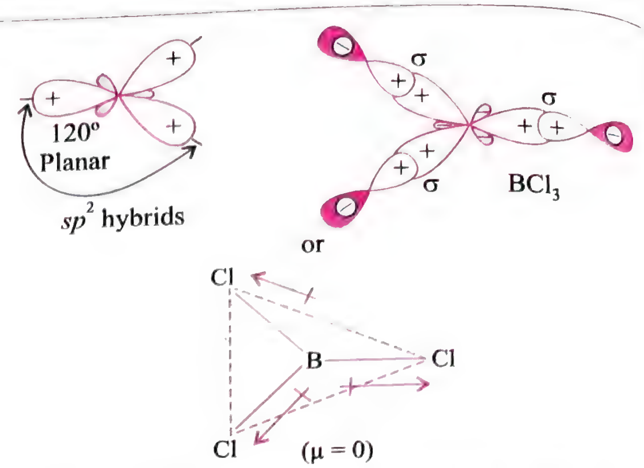


Fig. 2.23 Formation of sp^2 hybrids and the BCl_3 molecule

Each of the hybrid orbitals formed has one-third *s* character (33%) and two-third *p* character (67%). The non-participating *p* orbitals, if half-filled, can form a bond with other atoms having half-filled orbitals. For example, a few compounds in which sp^2 hybridisation takes place are as follows:

a. All compounds of boron, e.g. BF_3, BH_3 etc.

b. All compounds of carbon containing ($C = C$) double bond.

3. **Tetrahedral or sp^3 hybridisation:** When one *s*- and three *p*-orbitals belonging to the same shell of an atom mix together to form four new equivalent orbitals, the type of hybridisation is called sp^3 or tetrahedral hybridisation. The new orbitals are called sp^3 tetrahedral orbitals.

   These are directed towards the four corners of a regular tetrahedron and make an angle of 109° 28′ with one another as represented in Fig. 2.24.

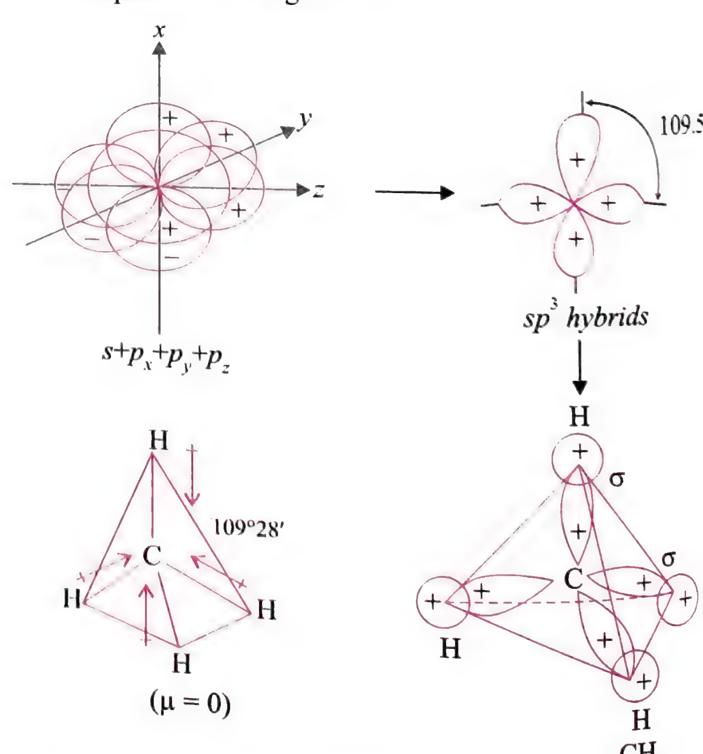


Fig. 2.24 Formation of sp^3 hybrids by the combination of s, p_x, p_y and p_z atomic orbitals of carbon and the formation of CH_4 molecule

Each sp^3 hybrid orbitals has 25% s character and 75% p character. For example, a few compounds in which sp^3 hybridisation occurs are methane (CH_4), ethane (C_2H_6) etc. where all compounds of carbon contain (C—C) single bonds only. Also, the size of sp hybrid orbital is smaller than that of sp^2 hybrid orbital which in turn is smaller than that of sp^3 hybrid orbital.

2.21.5 Geometry or Shapes of Molecules

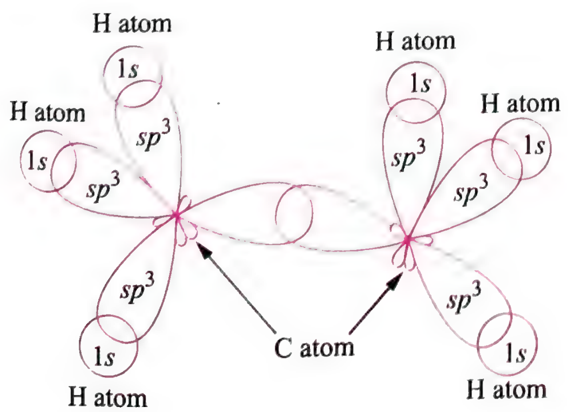
Ionic bond is non-directional and hence the structure of an ionic compound is determined by the relative size of its ions. However, a covalent bond is directional because it is formed by the overlapping of half-filled orbitals. The direction of overlap gives the direction of bond.

Note: A particular arrangement obtained by bonding a number of atoms in definite directions to the central atom of a molecule is called the geometry or shape of the molecule.

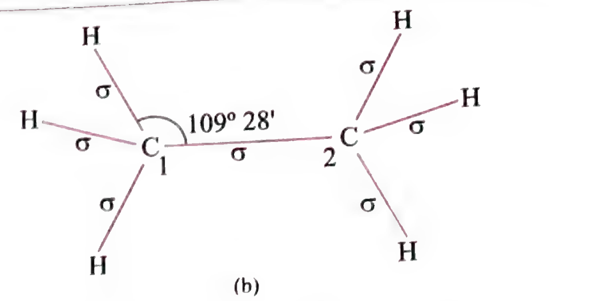
The geometry of shape of a molecule can be explained on the basis of the (i) hybridisation and (ii) valence shell electron pair repulsion theory.

2.21.6 Shapes of Molecules Containing Bond Pairs Only

1. **Shape of ethane (C_2H_6) molecule (sp^3 hybridisation):** In the formation of ethane molecule, each carbon atom undergoes sp^3 hybridisation, thus forming four sp^3 hybrid orbitals directed towards the corners of a tetrahedron and inclined to each other at an angle of 109° 28′. One sp^3 hybrid orbital of the first carbon atom undergoes overlapping with one sp^3 hybrid orbital of the second carbon atom along the internuclear axis, thus forming σ-bond between them. The remaining three sp^3 hybrid orbitals of each carbon atom undergo overlapping with the half-filled $1s$ orbitals of H atoms, each along the internuclear axis and hence forming σ-bond. Thus, the complete picture may be represented as shown in Fig. 2.25.



(a)



(b)

Fig. 2.25 Formation of ethane molecule

$$\begin{bmatrix} 1\,\sigma\,(C - C) \Rightarrow sp^3\,(C_1) - sp^3\,(C_2) \\ 6\,\sigma\,(C - H)\text{ bond} \Rightarrow sp^3\,(C) - 1s(H) \end{bmatrix}$$

2. **Shape of ethene (C_2H_4) molecule (sp^2 hybridisation):** The valence electronic configuration of C atom in the excited state C ($Z = 6$) is $2s^1 2p_z^{\,1}\, 2p_y^{\,1}\, 2p_x^{\,1}$.
In the formation of ethylene molecule, each C atom undergoes sp^2 hybridisation, thus leaving one $2p_x$ orbital in the original state, i.e. in the unhybridised state. Three sp^2 hybrid orbitals of each C atom are planar and are inclined to each other at an angle of 120°. One sp^2 hybrid orbital of the first C atom overlaps with one sp^2 hybrid orbital of the second C atom along the internuclear axis, thereby forming one sigma bond between them. The other two sp^2 hybrid orbitals of each C atom overlap with the half-filled $1s$ orbitals of H atoms along their respective internuclear axis forming σ-bonds. The unhybridised $2p_x$ orbital of the first C atom undergoes sideways overlapping with the unhybridised $2p_x$ orbital of the second C atom, thereby forming a π-bond between the two C atoms. So, the formation of ethylene molecule may be represented as shown in Figs. 2.26 and 2.27.

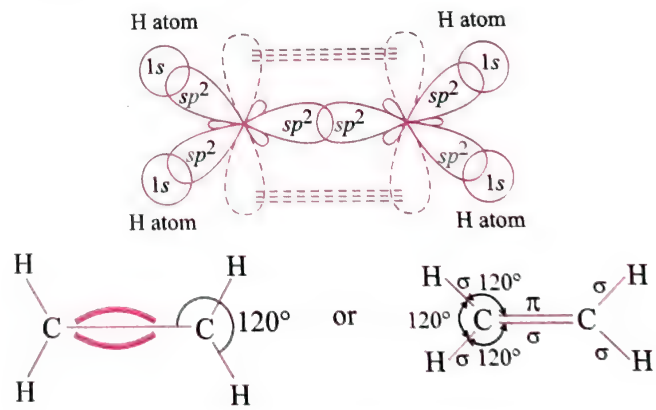
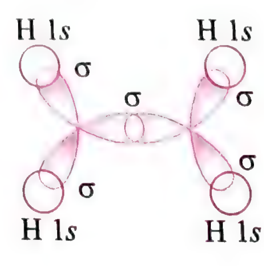


Fig. 2.26 Formation of ethene (C_2H_4) molecules



(a)

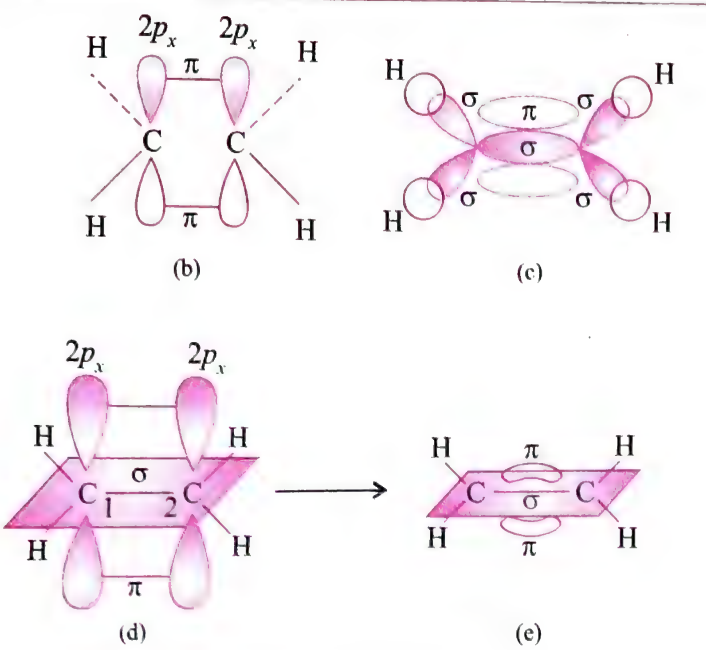


Fig. 2.27 Formation of σ- and π-bonds in ethene

$$\left[\begin{array}{l}\text{One } \sigma\text{ (C — C) bond} \Rightarrow sp^2\ (C_1) — sp^2(C_2)\\ \text{One } \pi\text{ (C = C) bond} \Rightarrow \text{pure } p\ (C_1) — \text{pure } p\ (C_2)\\ \quad 4\,\sigma\text{ (C — H) bond} \Rightarrow sp^2\ (C) — 1s\ (H)\end{array}\right]$$

3. **Shape of acetylene (C_2H_2) or ethyne molecule (*sp* hybridisation):** In the formation of acetylene molecule, each C atom undergoes *sp* hybridisation leaving two 2*p* orbitals in the original unhybridised state. The two *sp* hybrid orbitals of each C atom are linear, i.e. they are 180° apart. One *sp* hybrid orbital of the first C atom overlaps with one *sp* hybrid orbital of the second C atom along the internuclear axis, thus forming σ-bond between them. The second *sp* hybrid orbital of each C atom overlaps with the half-filled 1*s*-orbital of H atom again along the internuclear axis and thus forming σ-bonds. The unhybridised p_x orbital of the first C atom undergoes sideways overlapping with the p_x orbital of the second C atom, thereby forming a π-bond between two C atoms. Simillarly, the unhybridised p_y orbitals overlap sideways forming another π-bond between two C atoms. Thus, all the carbon and hydrogen atoms are linear and there is an electron cloud above and below, in the front and at the back of (C—C) axis. In other words, there is an electron cloud all around the internuclear axis, thus giving cylindrical shape as represented in Figs. 2.28 and 2.29(a), (b) and (c).

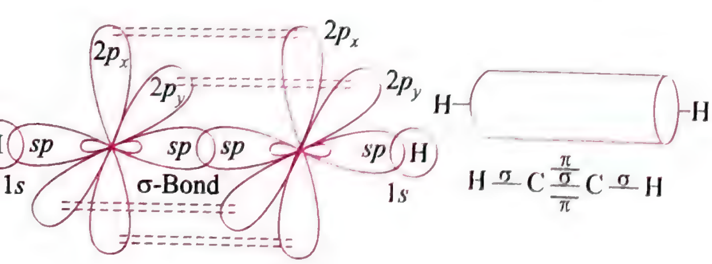


Fig. 2.28 Formation of acetylene (C_2H_2) molecule (cylindrical shape)

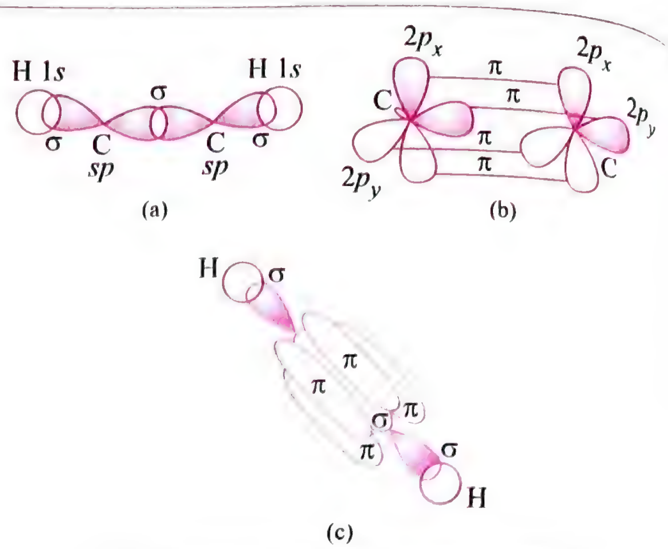


Fig. 2.29 Formation of σ- and π-bonds in acetylene

$$\left[\begin{array}{l}\text{One } \sigma\text{ (C — C) bond} \Rightarrow sp\ (C_1) — sp(C_2)\\ 2\pi\text{ (C} \equiv \text{C) bond} \Rightarrow \text{pure } p(C_1) — \text{pure } p(C_2)\\ \quad 2\sigma\text{ (C — H) bond} \Rightarrow sp(C) — 1\,s(H)\end{array}\right]$$

2.21.7 Hybridisation and Shapes of Molecules Containing Bond Pairs and Lone Pairs of Electrons

1. **Hybridisation bond angle and shape of NH_3 molecule (sp^3 hybridisation):** Valence electronic configuration of N (Z = 7) is $2s^2\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$. One 2*s* and three 2*p*-obritals undergo sp^3 hybridisation forming four sp^3 hybrid orbitals out of which three contain one electron each and take part in bond formation and the fourth sp^3 hybrid orbital contains a lone pair of electrons and hence cannot participate in the bond formation. The four sp^3 hybrid orbitals will obviously be directed towards the corners of a tetrahedron and hence the bond angle between any two sp^3 hybrid orbitals would be 109° 28′. Now, when the three sp^3 hybrid orbitals, each containing one electron only, overlap withy the 1 *s*-orbitals of H atoms to form NH_3, the expected H–N–H bond angle is 109° 28′. But experimentally, the bond angle in NH_3 is found to be 107°. The decrease in bond angle is due to the repulsion between *lp–bp* and *bp–bp*.

The presenee of *lp*'s in addition to *bp*'s in the molecule causes distortion in the geometry of the molecule.

a. **How to find out the distored shape (i.e. actual shape) of the molecule:** Cover the *lp*'s of electrons and view how the rest of the molecule looks like. In case of NH_3 after covering the *lp*'s, the rest of the molecule looks like a *pyramid*.

Therefore, such a shape is known as pyramid (or trigonal or triangular) in which the three H atoms form the triangular base of the pyramid with N atom at the apex.

Similar types of shape, bond angle and hybridisation are observed inPCl_3, NF_3 and $H_3O^{\oplus}$ etc.

Thus, formation of NH_3 molecule is represented diagrammatically in Fig. 2.30.

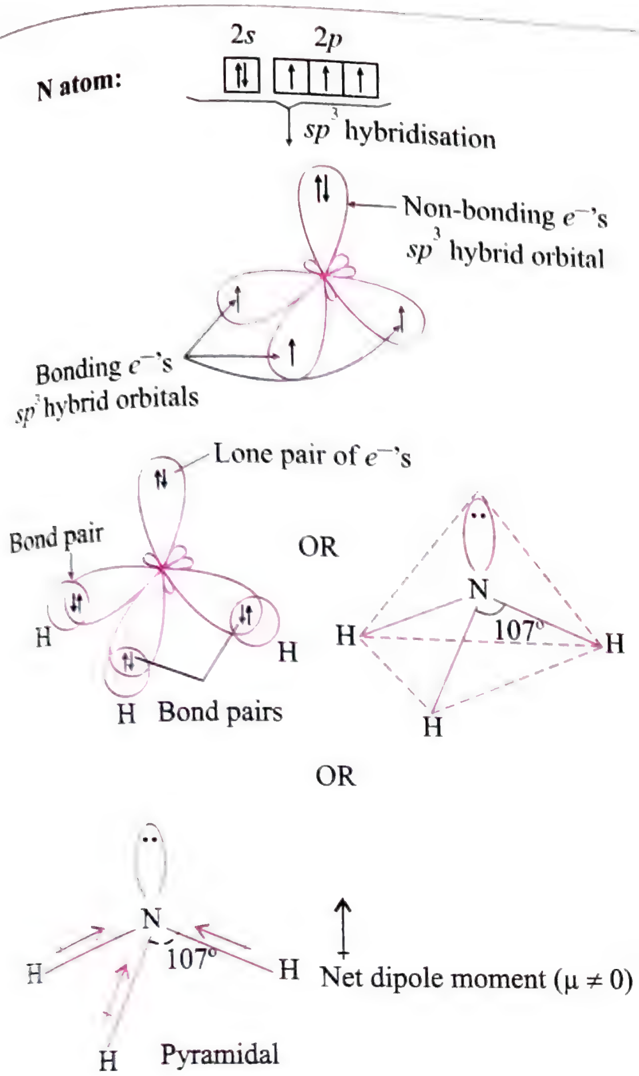


Fig. 2.30. Formation of ammonia (NH_3) molecule

Thus, we can have the following points.

i. Hybridisation (Hyb) of N in $NH_3 = sp^3$.

ii. Expected geometry (EG) in NH_3 = Tetrahedral (TH).

iii. Actual shape in NH_3 = Pyramidal.

iv. Expected bond angle (N – N – H) = 109° 28′.

v. Actual bond angle (H – N – H) = 107°.

vi. Three (C–H) bonds are formed by overlap of sp^3 (C) with 1s (H).

vii. One lone pair (*lp*) is present in vacant sp^3 hybrid orbital.

viii. $\mu \neq 0$.

ix. Whenever, lone pair e⁻'s are left, there is unequal distribution of *s*- character in hybrid orbitals.

2. **Hybridisation, bond angle and shape of H_2O molecule (sp^3 hybridisation):** Valence electronic configuraion of O atom (Z = 8) is $2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$.

One 2*s*- and three 2*p* orbitals undergo sp^3 hybridisation forming four sp^3 hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons (i.e. lone pair) each. The four sp^3 hybrid orbitals thus formed are directed towards the corners of a tetrahedron and hence the bond angle between any two sp^3 hybrid orbitals would be 109° 28′. Now when the two sp^3 hybrid orbitals containing one electron each, overlap with the half-filled 1*s* orbitals of H atoms to form H_2O, the expected H – O – H bond angle is 109° 28′. But experimentally the bond angle is found to be 104.5°.

The still lesser decrease in bond angle in H_2O than in NH_3 is due to repulsion of two lone pairs (2*lp*'s) with two bond pairs (2*bp*'s) and repulsion between *bp* and *bp*.

Hence more repulsion than that in NH_3, so lesser bond angle. The presence of *lp*'s in addition to *bp*'s in the molecule casues distortion in the geometry of the molecule.

a. **Predicting the actual shape of H_2O molecule:** After covering the 2 *lp*'s, the rest of the molecule looks like V-shaped or bent or angular shape.

Similar types of shape, bond angle and hybridisation are observed in OF_2, SO_2, NH_2, SCl_2 etc.

Thus, formation of H_2O molecule is represented diagrammatically in Fig. 2.31.

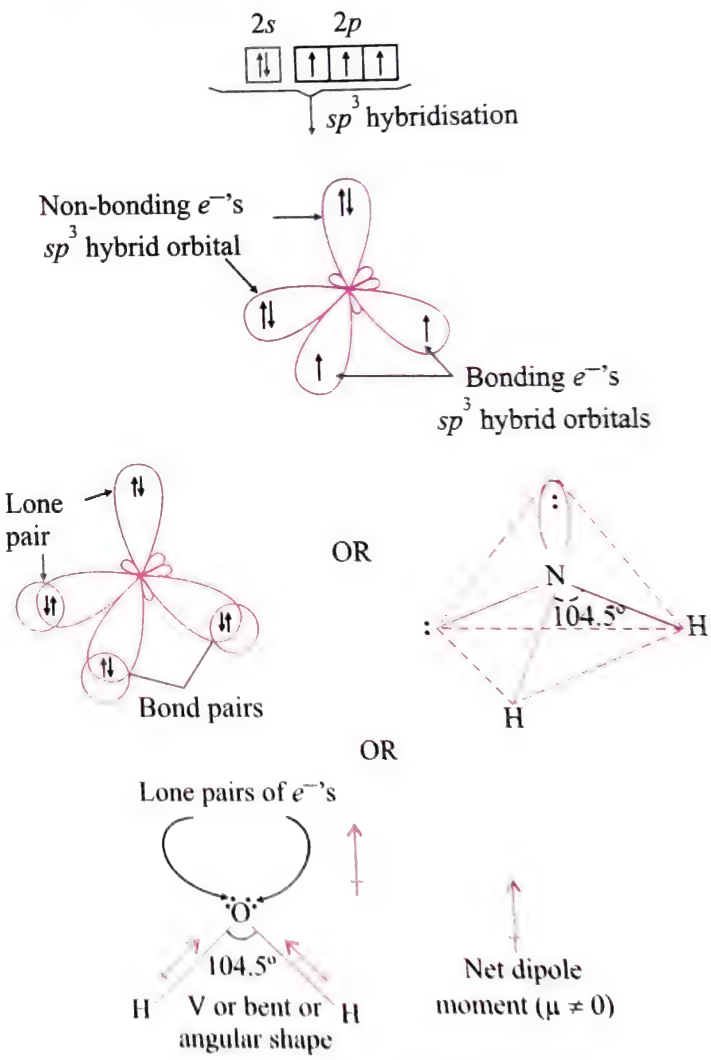


Fig. 2.31 Formation of water (H_2O) molecule

Thus, we can have the following points:

i. Hybridisation (Hyb) of O in $H_2O = sp^3$.

ii. Expected geometry (EG) in H_2O = Tertrahedral (TH).

iii. Actual shape in H_2O = V or bent or angular shape.

iv. Expected bond angle (H – O – H) = 109° 28′.

v. Actual bond angle (H – O –H) = 104.5°.

vi. Two (O–H) bonds are formed by overlap of sp^3 (O) with $1s$ (H).

vii. Two lone pairs (lp's) are present in the two vacant sp^3 hybrid orbitals.

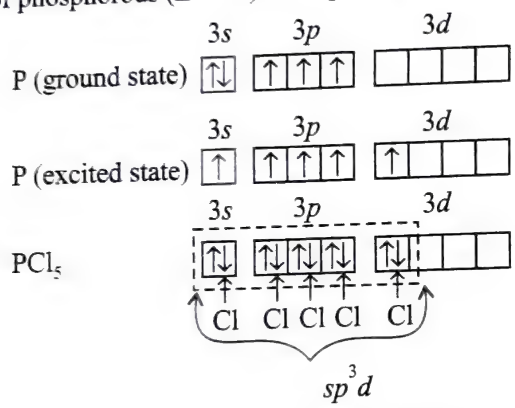
viii. $\mu \neq 0$.

ix. Unequal distribution of s-character in hybrid orbitals.

2.21.8 Hybridisation Involving *d*-ORBITALS

The elements present in the third period contain d orbitals in addition to s and p orbitals. The energy of the $3d$ orbitals is comparable to the energy of the $3s$ and $3p$ orbitals. The energy of $3d$ orbitals is also comparable to those of $4s$ and $4p$ orbitals. As a consequence, the hybridisation involving either $3s$, $3p$ and $3d$ or $3d$, $4s$ and $4p$ is possible. However, since the difference in energies of $3p$ and $4s$ orbitals is significant, no hybridisation invoving $3p$, $3d$ and $4s$ orbitals is possible.

1. **Formation of PCl_5 (sp^3d hybridisation):** The ground state and the excited state outer electronic configurations of phosphorous (Z = 15) are represented below.



sp^3d hybrid orbitals filled by electron pairs donated by five Cl atoms.

Now, the five orbitals (i.e. one s, three p and one d oritals) are available for hybridisation to yield a set of five sp^3d hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal as depicted in Fig. 2.32.

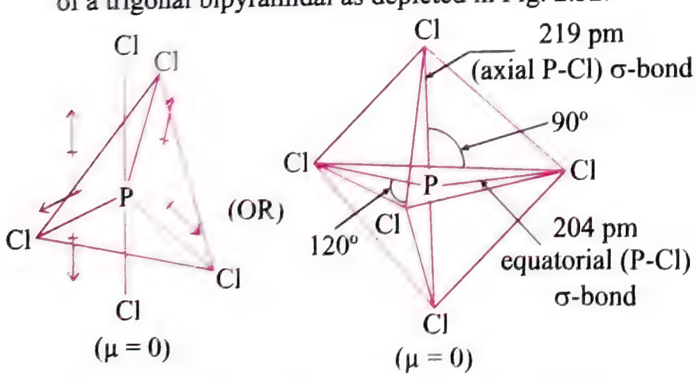


Fig. 2.32 Trigonal bipyramidal geometry of PCl_5 molecule

i. Hybridisation (Hyb) of P in $PCl_5 = sp^3d$.

ii. Shape = Trigonal bipyramid.

iii. Five (P – Cl) bonds are formed by the overlap of sp^3d (P) with $3p$ (Cl).

iv. $\mu = 0$.

v. Equal distribution of s-character in hybrid orbitals.

All the bond angles in trigonal bipyramidal geometry are not equivalent. In PCl_5 the five sp^3d orbitals of phosphorous overlap with the singly occupied p orbitals of chlorine atoms to form five (P – Cl) sigma bonds. Three P – C bonds lie in one plane and make an angle of 120° with each other, these bonds are termed as equatorial bonds. The remaining two (P – Cl) bonds–one lying above and the other lying below the equatorial plane, make an angle of 90° with the plane. These bonds are called axial bonds.

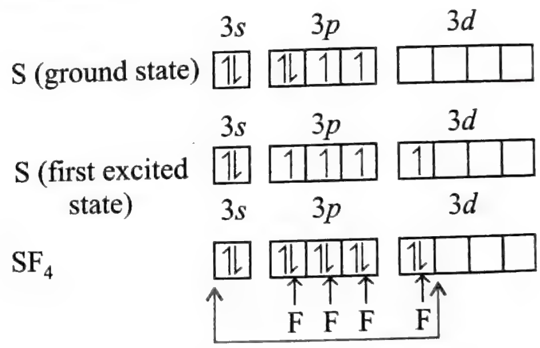
As the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs; therefore, axial bonds have been found to be slightly longer and hence slightly weaker than the equatorial bonds, which makes PCl_5 molecule more reactive.

That is why PCl_5(g) on heating gives PCl_3(g) and Cl_2(g).

$$PCl_{5(g)} \xrightarrow{\Delta} PCl_{3(g)} + Cl_{2(g)}$$

Other examples such as PF_5, $SbCl_5$, AsF_5 etc. show similar geometry, shape and bond angle.

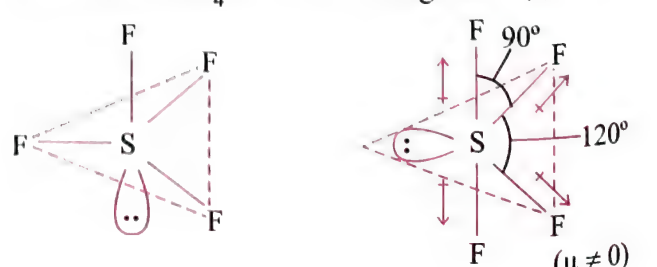
2. **Formation of SF_4 (sulphur tetra fluoride) molecule (sp^3d hybridisation):** SF_4 molecule contains one lone pair and four bond pairs of electrons. Valence electronic configuration of S (Z = 16) in ground state and first excited state is as shown below:



Formation of Sp^3d hybrid orbitals filled by electron pairs donated by 4S atoms.

It underegoes sp^3d hybridisation to form five hybrid orbitals to give a trigonal bipyramidal geometry in which one hybrid orbital contains one lone pair (lp) and the remaining four hybrid orbital contain one electron each which are shared with those of F atoms.

Depending upon the position occupied by lp, two possible structures of SF_4 are shown in Figs. 2.33 (a) and (b).



(a) (lp electrons present in axial position) (Less stable)

(b) (lp electrons present in equatorial position (More stable)

Fig. 2.33 (a and b) Two possible structures of SF_4

In Fig. 2.33 (a), there are three (lp–bp) repulsion at 90°. However, in Fig. 2.33 (b), there are only two (lp–bp) repulsions at 90°. Hence, (b) is more stable.

The shape shown in (b) is described as a *distorted tetrahedron (a folded square)* or *a see-saw*.

a. In SF_4 molecules:

i. Hybridisation (Hyb) of S in $SF_4 = sp^3d$.

ii. Expected geometry (EG) = Trigonal bipyramid (Tbp)

iii. Actual shape = See-saw

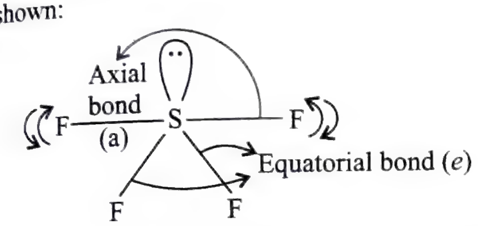
iv. 4 (S – F) σ-bonds are formed by overlap of sp^3d (S) with $2p$ (F).

v. One lp is present in vacant sp^3d hybrid orbital.

vi. $\mu \neq 0$.

vii. Unequal distribution of s-character is hybrid orbitals.

b. Predicting the actual shape of SF_4 molecule: After covering the lp, the rest of the molecule looks like see-saw as shown:



Bond length of axial (F – S) > equatorial (F – S) bond length that is why $SF_{4(g)}$ on heating gives $SF_{2(g)}$ and $F_{2(g)}$.

$$SF_{4(g)} \xrightarrow{\Delta} SF_{2(g)} + F_{2(g)}$$

Note:

i. In trigonal bipyramidal (Tbp) geometry, the molecules having 1, 2 and 3 lp's the actual shapes of molecules can be obtained by placing the lp's always on equatorial position.

ii. Repulsion between bp's decreases with increasing bond angle between them. Therefore, repulsion between bp and bp at 120° and 180° is very very less in comparison to those at 90°.

3. Formation of ClF_3 (chlorine trifluoride) molecule (sp^3d hybridisation): $:\ddot{Cl}F_3$ molecule contains two lp's and three bp's of electrons. Valence electronic configuration of Cl (Z = 17) in ground state and first excited states is as shown below:

Cl (ground state): 3s [⇅] 3p [⇅][⇅][↑] 3d [ ][ ][ ][ ][ ]

Cl (first excited state): 3s [⇅] 3p [⇅][↑][↑] 3d [↑][ ][ ][ ][ ]

ClF_3: 3s [⇅] 3p [⇅][⇅][⇅] 3d [⇅][ ][ ][ ][ ]
F F F

sp^3d hybridisation

It undergoes sp^3d hybridisation to form five hybrid orbitals to give a trigonal bipyramidal (Tbp) geometry.

Depending upon the position occupied by two lp's three possible arrangements are shown in Figs. 2.34. (a), (b) and (c).

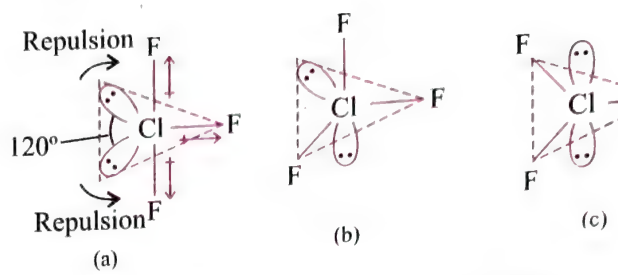


Fig. 2.34 Three possible structures of ClF_3

In Fig. 2.34 (a), the lp's are at equatorial position so there are less lp–bp repulsions as compared to others in which the lp's are at axial position. So, structure (a) is most stable.

Therefore, according to the VSEPR theory, Fig. 2.34 (a) has least repulsions and hence it has minimum energy and maximum stability.

a. In ClF_3 molecule:

i. Hybridisation (Hyb) of Cl in $ClF_3 = (sp^3d)$.

ii. Expected geometry (EG) = Trigonal bipyramid (Tbp).

iii. Actual shape = T or arrow shape.

iv. Three (Cl – F) σ-bonds are formed by the overlap of sp^3d (Cl) with $2p$ (F).

v. Two lp's are present in two vacant sp^3d hybrid orbital.

vi. $\mu \neq 0$.

vii. Unequal distribution of s-character in hybrid orbitals.

b. Predicting the actual shape of ClF_3 molecule: After covering the two lp's, the rest of the molecule looks like a (⊢). Hence it is T-shaped. But due to repulsion between lp on equatorial and bp (between Cl and F) at axial position, the T shape looks like an arrow (⟵) shape.

4. Formation of XeF_2 (Xenon difluoride) molecule (sp^3d hybridisation): $:\ddot{X}eF_2$ molecule contains three lp's and two bp's electrons. Valence electronic configuration of Xe (Z = 54) in ground state and first excited states is as shown below:

Xe (ground state): 5s [⇅] 5p [⇅][⇅][⇅] 5d [ ][ ][ ][ ][ ]

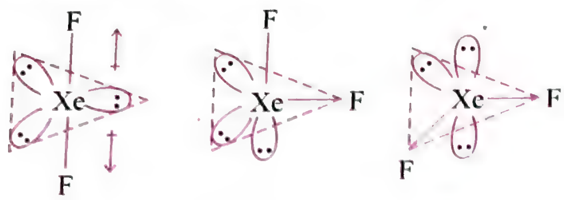
Xe (first excited state): 5s [⇅] 5p [⇅][⇅][↑] 5d [↑][ ][ ][ ][ ]

XeF_2: 5s [⇅] 5p [⇅][⇅][⇅] 5d [⇅][ ][ ][ ][ ]
F F

sp^3d hybridisation

It undergoes sp^3d hybridisation to form five hybrid orbitals to give a trigonal bipyramid (Tbp) geometry.

Depending upon the position occupied by three lp's the possible arrangements are shown in Figs. 2.35 (a), (b) and (c).



(a) Most stable (Linear shape) (b) Less stable (c) Less stable

Fig. 2.35 Three possible structures of XeF_2

As shown in the formation of ClF_3 [Figs. 2.34 (a), (b) and (c)], more stable geometry is that in which all the lp's are at equatorial position due to less repulsion of lp's at 120°.

a. In XeF_2 molecule:

i. Hybridisation (Hyb) of Xe in $XeF_2 = sp^3d$.

ii. Expected geometry (EG) = Trigonal bipyramid (Tbp).

iii. Actual shape = Linear.

iv. Two (Xe – F) σ-bonds are formed by the overlap of sp^3d (Xe) with $2p$ (F).

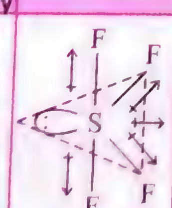
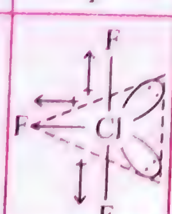
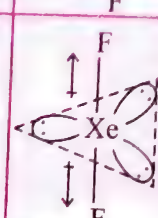
v. Three lp's are present in three vacant sp^3d hybrid orbitals.

vi. (μ) = 0.

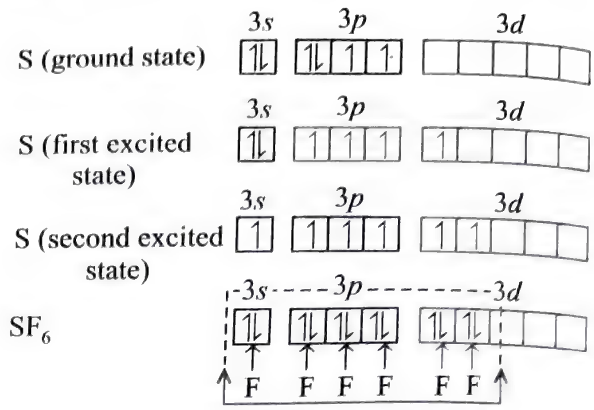
vii. Unequal distribution of s-character in hybrid orbitals.

b. Predicting the actual shape of XeF_2 molecule: After covering the three lp's, the rest of the molecule looks like a (F $\overleftrightarrow{\quad}$ Xe $\overleftrightarrow{\quad}$ F) linear molecule having dipole moment (μ) = 0. (see Table 2.10).

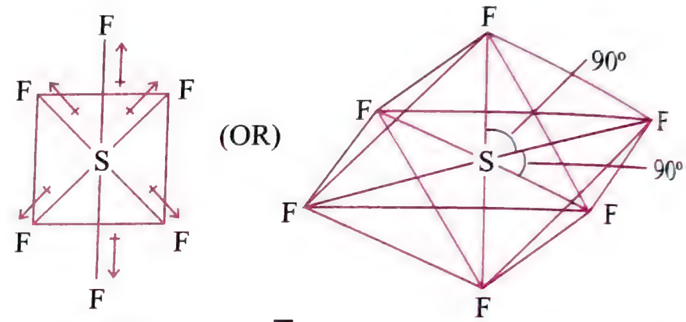
ble 2.10 Summary of shapes of the molecule having (Tbp) geometry containing 1, 2 and 3 lp's

olecule type	Example	No. of bp's	No. of lp's	Hybridisation and geometry	Structure	Shape and dipole
AB_4E	$\ddot{S}F_4$	4	1	sp^3d (Tbp)		See-saw or folded square or (distorted / irregular TH) $\mu \neq 0$
B_3E_2	$\ddot{Cl}F_3$	3	2	sp^3d (Tbp)		T or arrow (→) shape $\mu \neq 0$
B_2E_3	$:\ddot{Xe}F_2$	2	3	sp^3d (Tbp)		Linear $\mu = 0$

5. Formation of SF_6 (sulphur hexa fluoride) molecule (sp^3d^2 hybridisation): SF_6 molecule contains six, bond pairs of electrons. Valence electronic configuration of S (Z = 16) in ground state, first and second excited states is as shown below:



sp^3d^2 hybridisation



(μ = 0)

All (F–S–F) bond angles = 90°
All (S–F) bond length are equal

Fig. 2.36 Octahedral geometry of SF_6 molecule

a. In SF_6 molecules:

i. Hybridisation (Hyb) of S in $SF_6 = sp^3d^2$.

ii. Shape of SF_6 = Octahedron (OH).

iii. All bond angle (F – S – F) = 90°.

iv. Six (S – F) σ-bond are formed by the overlap of sp^3d^2 (S) with $2p$ (F).

v. μ = 0.

vi. Equal distribution of s-character in hybrid orbitals.

The available six orbitals, i.e. one s, three p and two d are singly occupied by electrons. These orbitals hybridise to form six new sp^3d^2 hybrid orbitals which are projected towards the six corners of a regular octahedron in SF_6. These six sp^3d^2 hybrid orbitals overlap with singly occupied $2p$ orbitals of F atoms to form six (S – F) sigma (σ) bonds.

Thus, SF_6 molecule has an octahedral (OH) geometry as shown in Fig. 2.36.

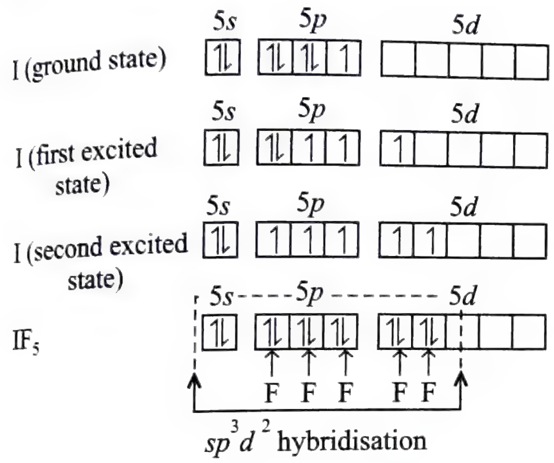
In SF_6, four (S – F) σ-bonds are in the same plane at 90° to one another and are directed towards the four corners of a square. The other 2F atoms are also at 90° above and below the plane of F atoms.

SF_6 molecule is a symmetrical molecule and, therefore, is stable and far less reactive than SF_4 and PCl_5.

That is why, SF_6 does not dissociate on heating since all the six (S – F) bonds are equal in bond strength and bond lengths. For example, Te $(OH)_6$, SeF_6 and Te F_6 also have regular octahedral geometry (OH).

6. **Formation of IF_5 (interhalogen compound) molecule (sp^3d^2 hybridisation):** :IF_5 (interhalogen compound) contains five *bp*'s and one *lp* of electrons.

Valence electronic configuraion of I (Z = 53) in ground state, first and second excited states is as shown below:



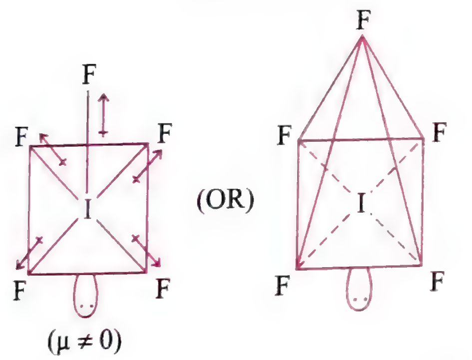


Fig. 2.37 Square pyramid geometry of IF_5 molecule

a. **In IF_5 molecule:**

i. Hybridisation (Hyb) of I in $IF_5 = sp^3d^2$.

ii. Expected geometry (EG) = Octahedral (OH).

iii. Actual shape = Square pyramid.

iv. 5 (I – F) σ-bonds are formed by the overlap of sp^3d^2 (I) with 2*p* (F).

v. One *lp* is present in the vacant sp^3d^2 hybrid orbital.

vi. $\mu \neq 0$.

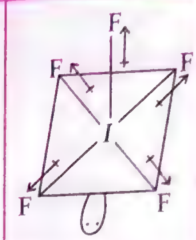
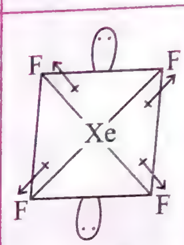
vii. Unequal distribution of *s*-character in hybrid orbitals.

It undergoes sp^3d^2 hybridisation to form six hybrid orbitals to give an octahedral geometry.

The presence of *lp* in addition to *bp*'s in the molecule causes distortion in the geometry of the molecule.

b. **Predicting the actual shape of the molecule:** After covering the one *lp*, the rest of molecule looks like square pyramid, having dipole moment ($\mu \neq 0$).

Table 2.11 Summary of shapes of the molecule having octahedral geometry (OH) containing one and two *lp*'s

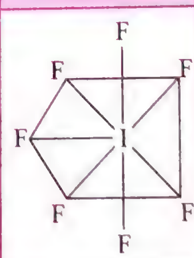
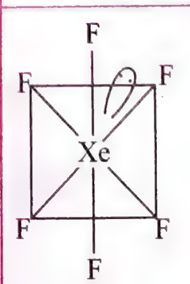
Molecule type	Example	No. of *bp*'s	No. of *lp*'s	Hybridisation and geometry	Structure	Shape and dipole moment
AB_5E	:IF_5	5	1	sp^3d^2 (OH)		Square pyramid $\mu \neq 0$
AB_4E_2	:XeF_4	4	2	sp^3d^2 (OH)		Square planar $\mu = 0$

Note:

i. Unlike trigonal bipyramid (Tbp) geometry, in octahedral (OH) and pentagonal bipyramid (Pbp) geomety, the actual shape of the molecule can be obtained by putting the lp's always on axial position.

ii. The repulsion between bp–bp, bp–lp and lp–lp at 72° in Pbp is more in comparison to those at 90°.

Table 2.12 Summary of shapes of the molecules having pentagonal bipyramid (Pbp) geometry containing zero and one *lp*

Molecule type	Example	No. of *bp*'s	No. of *lp*'s	Hybridisation and geometry	Structure	Shape and dipole moment
AB_7	IF_7	5	0	sp^3d^3 (Pbp)		Pbp $\mu = 0$
AB_6E	:XeF_6	6	1	sp^3d^3 (Pbp)		It should be pentagonal pyramid but it is distorted OH or monocapped OH ($\mu \neq 0$)

2.21.9 Some Rules for Predicting Hybridisation and Shapes of Molecules/Ions

First method:

Step 1: Select the central atom and find to which group it belongs.

Step 2: Find the number of valence electrons (V) in the central atom. For example, group 13 to group 18 contains 3, 4, 5, 6, 7, 8 electrons respectively.

Note: Group 1 and 2 elements are ionic compounds (except compounds of Be, e.g. $BeCl_2$) thus these elements do not undergo hybridisation.

Step 3: Calculate the number of monovalent (M) atoms attached to the central atom.

Step 4: For neutral molecules:

$$\text{Hybridisation (Hyb)} = \frac{1}{2}(V+M) = X \left(\begin{array}{l}\text{Sum of orbitals}\\ \text{involved in}\\ \text{hybridisation}\end{array}\right)$$

The type of hybridisation is decided by the value of X as follows:

Type of hybridisation	sp	sp^2	sp^3 or dsp^2	sp^3d or dsp^3	sp^3d^2 or d^2sp^3	sp^3d^3 or d^3sp^3
Value of X (i.e., sum of orbitals involved in hybridisation)	1+1 = (2)	1+2 = (3)	1+3 = (4) or 1+1+2 = (4)	1+3+1 = (5) or 1+1+3 = (5)	1+3+2 = (6) or 2+1+3 = (6)	1+3+3 = (7) or 3+1+3 = (7)

For cations:

$$\text{Hyb} = \frac{1}{2}\left[(V+M)-(\text{No. of +ve charge on cation})\right] = X$$

For anions:

$$\text{Hyb} = \frac{1}{2}\left[(V+M)+(\text{No. of -ve charge on anion})\right] = X$$

Limitation: This method cannot predict the shape of the molecule/ion, containing lp's.

Examples:

1. $NH_3 \Rightarrow X = \frac{1}{2}(V+M) = \frac{1}{2}(5+3) = 4$

   $\therefore$ Hybridisation $= sp^3$

2. $H_2O \Rightarrow \text{Hyb} = X = \frac{1}{2}(V+M) = \frac{1}{2}(6+2) = 4 = sp^3$

3. $NO_3^{\ominus}$ ion $\Rightarrow \text{Hyb} = X = \frac{1}{2}(V+M+1) = \frac{1}{2}(5+0+1)$

   $= 3 = sp^2$

Note: Oxygen is a bivalent element hence M = 0.

4. $\overset{\oplus}{N}H_4 \Rightarrow \text{Hyb} = X = \frac{1}{2}(V+M-1) = \frac{1}{2}(5+4-1) = 4$

   $= sp^3$

5. $SF_4 \Rightarrow \text{Hyb} = X = \frac{1}{2}(V+M) = \frac{1}{2}(6+4) = 5 = sp^3d$

6. $XeOF_4 \Rightarrow \text{Hyb} = X = \frac{1}{2}(V+M) + \frac{1}{2}(8+4+0) = 6$

   $= sp^3d^2$

7. $XeF_6 \Rightarrow \text{Hyb} = X = \frac{1}{2}(V+M) = \frac{1}{2}(8+6) = 7 = sp^3d^3$

Second method:

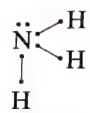
Step 1: Select the central atom and find the number of valence electron in it.

Step 2: Draw the Lewis structure of the molecule/ion.

Step 3: Calculate the number of bp's and lp's in the molecule. The sum of bp's and lp's is called steric number (SN). Therefore, hybridisation = SN = X.

This method can predict the shapes of the molecules/ions containing lp of electron also.

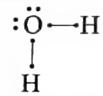
Examples:

1. $NH_3 \Rightarrow$ 

   X = Hyb = SN = 3bp + 1 lp = 4 = sp^3

   Geometry = Tetrahedral (TH)

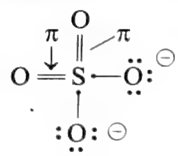
   Shape: Covering the lp's, the rest of the molecule looks like a *pyramid*.

2. $H_2O \Rightarrow$ 

   X = Hyb = SN = 2 bp + 2lp = 4 = sp^3

   Geometry = TH

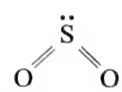
   Shape: Covering two lp's shape is V or bent shape.

3. SO_4^{2-} ion $\Rightarrow$ 

   X = Hyb = SN = 4 bp + zero lp = 4 = sp^3

   Note: π bond is excluded in hybridisation.

   Since central atom (S) in SO_4^{2-} does not have lp's so its geometry and shape is same, i.e. tetrahedral (TH).

4. $\ddot{S}O_2 \Rightarrow$ 

   X = Hyb = SN = 2bp + 1lp = 3 = sp^2

   Geometry = Planar

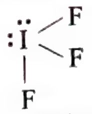
   Shape: Covering one lp, shape is V or bent shape.

5. :Ï F ⇒ :Ï – F

   X = Hyb = SN = 1bp + 3 lp = 4 = sp^3

   Geometry = TH

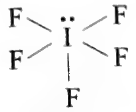
   Shape: Covering three lp's shape is linear.

6. $\ddot{\text{I}}F_3 \Rightarrow$ 

X = Hyb = SN = $3bp + 2lp = 5 = sp^3d$

Geometry = Triangular bipyramid (Tbp).

Shape: Covering two lp's shape is T-shape or arrow shape.

7. $\ddot{\text{I}}F_5 \Rightarrow$ 

X = Hyb = SN = 5bp + $1lp = 6 = sp^3d^2$

Geometry = Octahedral

Shape: Covering one lp, shape is square pyramid.

Third method: Rules for determining geometry of molecule/ion:

Step 1: No. of electron pairs = No. of atom bonded + $\frac{1}{2}$ (Group no. of atom – No. of valence e^- involved in bonding) = X = Hyb.

Step 2: For cation: No. of e^- pairs = No. of atom bonded + $\frac{1}{2}$ (Group no. of atom – no. of valence e^- involved in bonding – (positve charge on cation) = X = Hyb

Step 3: For anions: No. of e^- pairs = No. of atom bonded + $\frac{1}{2}$ (Group no. of atom – No. of valence e^- involved in bonding + (Negative charge on anion) = X = Hyb

Examples:

1. $NH_3 \Rightarrow 3 + \frac{1}{2}(5-3) = 4 = X = \text{Hyb} = sp^3$
2. $SF_4 \Rightarrow 4 + \frac{1}{2}(6-4) = 5 = X = \text{Hyb} = sp^3d$
3. $PCl_5 \Rightarrow 5 + \frac{1}{2}(5-5) = 5 = X = \text{Hyb} = sp^3d$
4. $BF_4^{\ominus} \Rightarrow 5 + \frac{1}{2}(3-4+1) = 4 = X = \text{Hyb} = sp^3$
5. $NO_2^{\ominus} \Rightarrow 2 + \frac{1}{2}(5-4+1) = 3 = X = \text{Hyb} = sp^2$
6. $\overset{\oplus}{N}H_4 \Rightarrow 4 + \frac{1}{2}(5-4-1) = 4 = X = \text{Hyb} = sp^3$
7. $NO_3^{\ominus} \Rightarrow 3 + \frac{1}{2}(5-6+1) = 3 = X = \text{Hyb} = sp^2$

Fourth method: Predicting the type of hybridisation of the central atom.

Step 1: Add the number of valence electrons of all the atoms present in the given molecule/ion.

Step 2: If the given ion is a cation, subtract the number of electrons equal to the charge on the cation. If the given ion is an anion, add the number of electrons equal to the charge on the anion.

Step 3: **i.** If the result obtained in step 2 is ≤ 8, divide it by 2 and find the sum of the quotient and remainder.

ii. If the result obtained in step 2 is 9 to 56, divide by 8 and find the first quotient (Q_1). Divide the remainder R_1 (if any) by 2 and find the second quotient (Q_2). Add all the quotients and the final remainder (R_2).

The final result obtained in (i) or (ii) is X. The type of hybridisation is decided by the value of X.

Examples:

1. **H_2O:**

Total valence electrons = 2 + 6 = 8

$X = \frac{8}{2} = 4 + 0 = 4$

Hybridisation = sp^3

2. **$NO_3^{\ominus}$ ion:**

Total valence electrons = 5 + 3 × 6 = 23

Charge = – 1

Hence, after adding 1, result = 24.

$\frac{24}{8} = 3\,(Q_1) + 0\,(R_1), X = 3$

Hybridisation = sp^2

3. **SO_2:**

Total valence electrons = 6 + 2 × 6 = 18

$\frac{18}{8} = 2\,(Q_1) + 2\,(R_1),\ \frac{2}{2} = 1(Q_2) + 0\,(R_2),$

$X = 2 + 1 + 0 = 3$

Hybridisation = sp^2

4. **SF_6:**

Total valence electrons = 6 + 6 × 7 = 48

$\frac{48}{8} = 6\,(Q_1) + 0\,(R_1),\ X = 6$

Hybridisation = $sp^3\,d^2$

5. **CO_3^{2-} ion:**

Total valence electrons = 4 + 3 × 6 = 22

Charge = –2

Hence, after adding 2, result = 24.

$\frac{24}{8} = 3\,(Q_1) + 0\,(R_1), X = 3$

Hybridisation = sp^2

6. **PCl_5:**

Total valence electrons = 5 + 5 × 7 = 40

$\frac{40}{8} = 5\,(Q_1) + 0\,(R_1),\ X = 5$

Hybridisation = sp^3d

7. **CO_2:**

Total valence electrons = 4 + 2 × 6 = 16

$\frac{16}{8} = 2\,(Q_1) + 0\,(R_1),\ X = 2$

Hybridisation = sp

8. **$ClO_4^{\ominus}$ (Perchlorate ion):**

Total valence electrons = 7 + 4 × 6 = 31

Charge = –1

Hence, after adding 1, result = 32.

$\frac{32}{8} = 4\,(Q_1) + 0\,(R_1)$, Hence, $X = 4$

Hybridisation = sp^3

9. **IF_7:**

Total valence electrons = $7 + 7 \times 7 = 56$

$\frac{56}{8} = 7\,(Q_1) + 0\,(R_1),\ X = 7$

Hybridisation = sp^3d^3

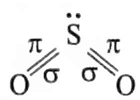
Predicting the shapes of molecules/ions: The shape is predicted by covering the hybrid orbitals containing the *lp*'s and then view the rest of the molecule how it looks like, which tells the shape of molecule/ions.

2.21.10 Hybridisation of Elements Involving π Bonds, Determination of Number of ($p\pi$–$p\pi$) and ($p\pi$ – $d\pi$) Multiple Bonds

π bond is formed due to sidewise overlap of two pure *p*-orbitals. In case of carbon–carbon (C–C) single, double (C=C) and triple (C≡C) bonds, the hybridisations are sp^3, sp^2 and *sp* respectively. Since C (Z = 6) is an element of 2nd period and it does not contain *d*-orbitals, so, (C=C) and (C≡C) compounds form ($p\pi$–$p\pi$) multiple bonds only.

The elements present in 3rd period contains *d*-orbitals in addition to *s* and *p* orbitals. Thus, these elements containing double bonds can form ($p\pi$–$d\pi$) multiple bonds in addition to ($p\pi$–$p\pi$) multiple bonds. For example,

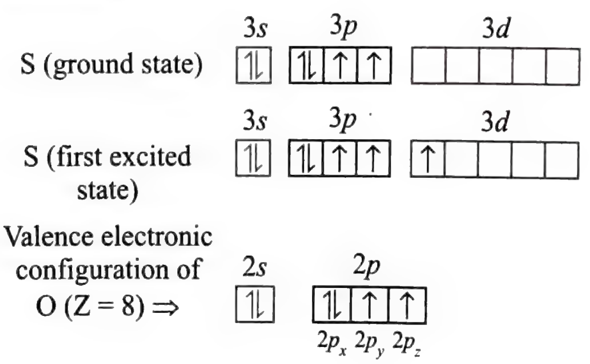
1. **Formation of ($p\pi$–$p\pi$) and ($p\pi$–$d\pi$) multiple bonds in SO_2 molecule:**

a. Structure of SO_2 molecule: 

SO_2 molecule contains one *lp*, two σ and 2π bonds. Formation of π bonds can be either ($p\pi$–$p\pi$) or ($p\pi$–$d\pi$) or both depending upon the presence of *d*-orbitals.

For the formation of 2σ and 2π bonds, S atom must have 4 e^-'s in its valence shell, which can be obtained from its first excited state.

Therefore, valence electronic configuration of *S* (Z = 16), in ground state and first excited state is shown as below.



b. The hybridisation of central atom (S) in SO_2 is determined either by the 1st or by 2nd method (refer to Section 2.21.9).

By 1st method: Hybridisation = $\frac{1}{2}(V + M) = \frac{1}{2}$

$= (6 + 0) = 3 = X = sp^2$

By 2nd method: Hybridisation = 2 *bp*

(only σ-bond) + 1 *lp* = 3 = *X* = sp^2

Thus, geometry of SO_2 is planar and shape is V or bent shape.

c. When one 3*s* orbital (containing one *lp*) and two 3*p* orbitals of S and atom on mixing forms three sp^2 hybrid orbitals leaving one pure *p*-orbital in 3*p* and one pure *d*-orbital in 3*d*. These two pure orbitals overlap with the two 2*p* orbitals of O atom and thus forms one ($p\pi$–$p\pi$) and one ($p\pi$–$d\pi$) multiple bonds as shown in Fig. 2.38.

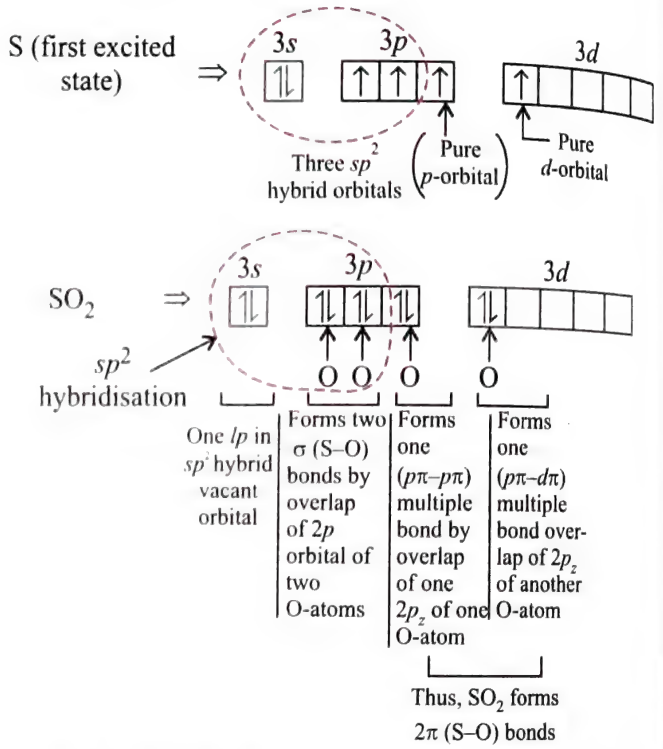


Fig. 2.38. Hybridisation and number of ($p\pi$–$p\pi$) and ($p\pi$–$d\pi$) multiple bonds in SO_2 molecule

d. **Summary:** Thus, in SO_2 molecule,

i. Number of ($p\pi$–$p\pi$) multiple bond = 1

ii. Number of ($p\pi$–$d\pi$) multiple bond = 1

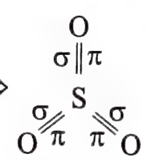
iii. Hybridisation = sp^2

iv. Geometry = Planar

v. Shape = V or bent or angular.

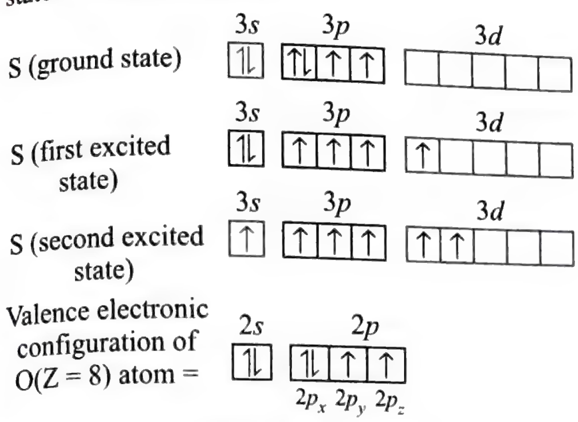
vi. $\mu \neq 0$

2. **Formation of ($p\pi$–$p\pi$) and ($p\pi$–$d\pi$) multiple bond in SO_3 molecule:**

a. Structure of SO_3 ⇒ 

SO_3 molecule contains 3σ and 3π bonds. For the formation 3σ and 3π bonds, S atom must have six e^-'s in its valence shell, which can be obtained from its second excited state.

Therefore, valence electronic configuration of S (Z = 16), in ground state, first and second excited states is shown as below:



b. **Determination of hybridisation of S atom in SO_3 molecule:**

By 1st method: Hybridisation = $\frac{1}{2}(V+M) = \frac{1}{2}$
$= (6 + 0) = 3 = X = sp^2$

By 2nd method: Hybridisation = 3 bp (only σ-bonds) + zero lp = 3 = $X = sp^2$

Since no lp's are present in SO_3, the geometry and shape is same, i.e. planar.

c. When one 3s orbital and two 3p orbitals of S atom on mixing forms three sp^2 hybrid orbitals leaving one pure p-orbital in 3p and two pure d-orbitals in 3d. These pure orbitals overlap with the three 2p orbitals of O atom and thus forms one ($p\pi$–$p\pi$) and two ($p\pi$–$d\pi$) multiple bond as shown in Fig. 2.39.

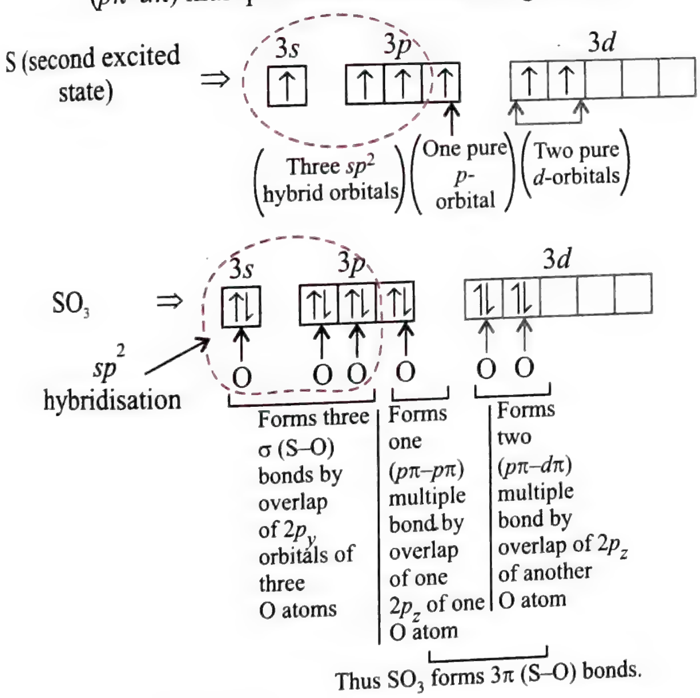


Fig. 2.39. Hybridisation and number of ($p\pi$–$p\pi$) and ($p\pi$–$d\pi$) multiple bonds in SO_3 molecule

d. **Summary:** Thus, in SO_3 molecule:

i. Number of ($p\pi$–$p\pi$) multiple bond = 1

ii. Number of ($p\pi$–$d\pi$) multiple bond = 2

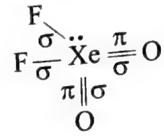
iii. Hybridisation = sp^2

iv. Geometry and shape = Planar

v. $\mu = 0$

3. **Formation of ($p\pi$–$p\pi$) and ($p\pi$–$d\pi$) multiple bonds in XeO_2F_2 (Xenondioxy difluoride) molecule:**

a. Structure of $\ddot{X}eO_2F_2$ molecule:



XeO_2F_2 molecule contains one lp, four σ and two π bonds and for the formation of these bonds, Xe atom must have six e^-'s in its valence shell, which can be obtained from its third excited state.

Therefore, valence electronic configuration of Xe (Z = 54) in ground state, first, second and third excited states are as follows:

Xe (ground state) = $5s^2, 5p^6, 5d^0$

Xe (first excited state) = $5s^2, 5p^5, 5d^1$

Xe (second excited state) = $5s^2, 5p^4, 5d^2$

Xe (third excited state) = $5s^2, 5p^3, 5d^3$

O (Z = 8) = $2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

F(Z = 9) = $2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$

b. **Determination of hybridisation of Xe atom in XeO_2F_2 molecule:**

By 1st method: Hybridisation = $\frac{1}{2}(V+M)$
$= \frac{1}{2}(8 + 2 + 0) = 5 = X = sp^3d$

By 2nd method: Hybridisation = 4 bp (only σ-bonds) + 1 lp = 5 = $X = sp^3d$

Thus, geometry of XeO_2F_2 is triangular bipyramid (Tbp) and shape is see-saw as shown in Fig. 2.40.

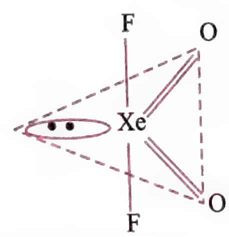


Fig. 2.40 Geometry and shape of XeO_2F_2 molecule

Note:

i. One lp in Tbp geometry must be on equatorial position for less repulsion and maximum stability.

ii. Most EN element must be on axial position thus out of O and F, F is most EN element and thus is placed at axial position.

Geometry of XeO_2F_2 = Tbp (sp^3d hybridisatin) shape of XeO_2F_2 = See-saw shape.

c. When one 5s-orbital (containing one lp), three 5p-orbitals and one 5d-orbitals of Xe atom on mixing forms five sp^3d hybrid orbitals leaving two pure 5d-orbitals. These two pure d-orbitals overlap with the two 2p-orbitals of O atom and thus forms two ($p\pi$–$d\pi$) multiple bond as shown in Fig. (2.41).

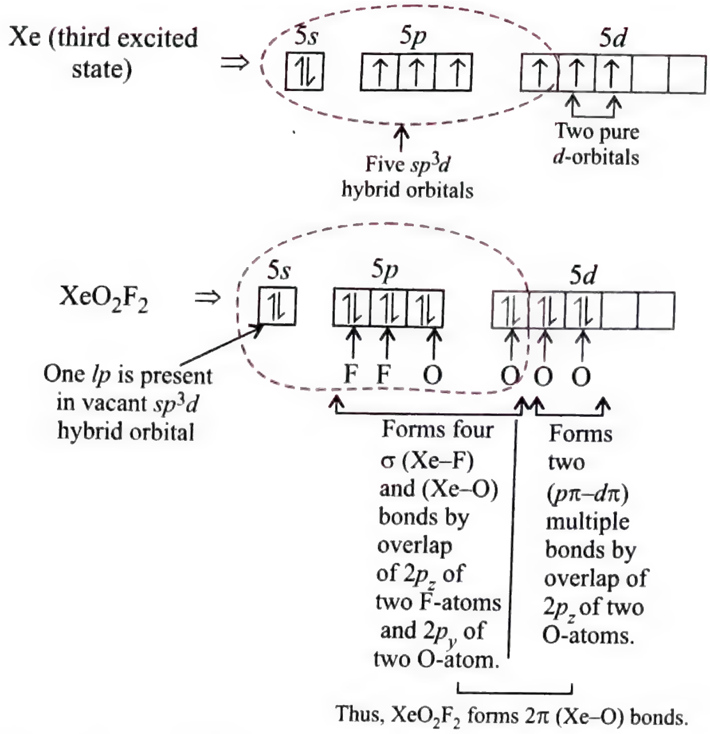


Fig. 2.41 Hybridisation and number of ($p\pi$–$p\pi$) and ($p\pi$–$d\pi$) multiple bonds in XeO_2F_2 molecule

d. Summary: Thus, in XeO_2F_2 molecule:

i. Number of ($p\pi$–$p\pi$) multiple bond = zero

ii. Number of ($p\pi$–$d\pi$) multiple bond = 2

iii. Hybridisation = sp^3d

iv. Geometry = Trigonal bipyramid (Tbp)

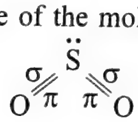
v. Shape = see-saw

vi. $\mu \neq 0$

4. Direct method to calculate the number of ($p\pi$–$p\pi$) and ($p\pi$–$d\pi$) multiple bonds in a molecule/ion.

a. Number of ($p\pi$–$p\pi$) and ($p\pi$–$d\pi$) multiple bonds can be calculated directly as follows:

Step 1: Write the structure of the molecule/ion. For example, $SO_2 \Rightarrow$



Step 2: Calculate the number of unpaired e^-'s required in bonding which is equal to the number of ($\sigma + \pi$) bonds, e.g. in SO_2.

No. of e^-'s required for bond formation = ($2\sigma + 2\pi$) = 4 e^-'s.

Step 3: Check which excited state of valence electronic configuration of central atom contains the number of electrons required for bond formation, e.g. in SO_2.

S (ground state) = $3s^2\,3p^2_x\,3p^1_y\,3p^1_z$ (2 e^-'s for bond formation)

S (first excited state) = $3s^2\,3p^1_x\,3p^1_y\,3p^1_z\,3d^1_{xy}$ (4 e^-'s for bond formation)

Step 4: Find out the hybridisation of central atom of the molecule/ion, e.g. in SO_2

Hybridisation = $(V + M) = \frac{1}{2}(6 + 0) = 3 = sp^2$

$= X$

Step 5: Mark the sp^2 hybridisation and then calculate the number of pure p and pure d-orbitals left, which gives the number of ($p\pi$–$p\pi$) and ($p\pi$–$d\pi$) multiple bond in the molecule/ion. For exmple, in SO_2.

$3s^2$ $3p^1_x$ $3p^1_y$	$3p^1_z$ $3d^1_{xy}$
For sp^2 hybridisation	One pure p and one pure d are left

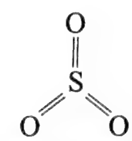
Forms one ($p\pi$–$p\pi$) and one ($p\pi$–$d\pi$) bonds

Hence, number of ($p\pi$–$p\pi$) multiple bond = 1 and number of ($p\pi$–$d\pi$) multiple bond = 1.

Examples:

i. SO_3:

- $SO_3 \Rightarrow$



($3\sigma + 3\pi$) = 6 e^- for bond formation.

- S (2nd excited state) = $3s^1\quad 3p^1_x\,3p^1_y\,3p^1_z\quad 3d^1_{xy}\,3d^1_{yz}$
  (six e^-'s for bond formaiton)

- Hybridisation = $\frac{1}{2}(V + M) = \frac{1}{2}(6 + 0) = 3$
  $= sp^2 = X$

- $3s^3\quad 3^1p_x\,3p^1_y\quad 3p^1_z\,3d^1_{xy}\,3d^1_{yz}$

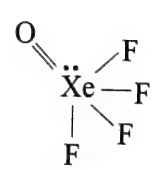
  sp^2 hybridisation   One pure p and two pure d-orbitals are left

  No. of ($p\pi$–$p\pi$) multiple bonds = 1

  No. of ($p\pi$–$d\pi$) multiple bonds = 2

ii. $XeOF_4$:

- $XeOF_4 \Rightarrow$



($5\sigma + 1\pi$) = 6 e^- for bonds formation.

- Xe (ground state) $\Rightarrow 5s^2\,5p^2_x\,5p_y^{\,2}\,5p_z^{\,2}$
  Xe (3rd excited state)

$\Rightarrow$ | $5s^2$ $5p^1_x$ $5p^1_y$ $5p^1_z$ | $5d^1_{xy}$ $5d^1_{yz}$ $5d^1_{zx}$ |

Six e^-'s for bond formation

- Hybridisation $= \frac{1}{2}(V + M) = \frac{1}{2}(8 + 4 + 0) = 6$

  $= sp^3d^2 = X$

- $\boxed{5s^2}\ \boxed{5p^1x\ \ 5p^1y\ \ 5p^1z}\ \boxed{5d^1xy\ \ 5d^1yz}\ \ 5d^1zx$

  sp^3d^2 hybridisation — One pure d-orbital is left

No. of ($p\pi$–$p\pi$) bonds = 0

No. of ($p\pi$–$d\pi$) bonds = 1

iii. XeO_3

- $XeO_3 \Rightarrow O{=}\ddot{X}e{=}O$ (with $=O$ below Xe)

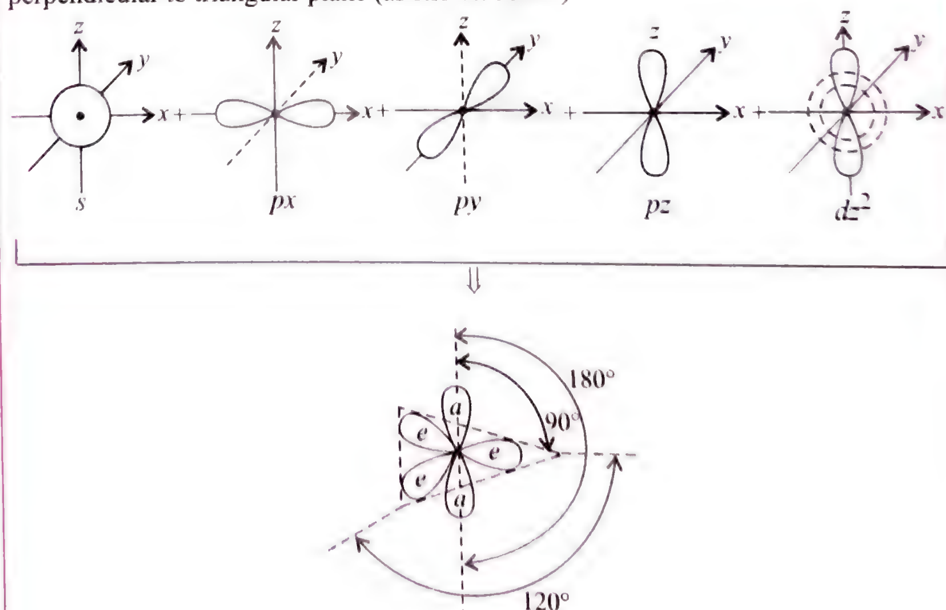
  $(3\sigma + 3\pi) = 6\ e^-$'s for bond formation
- Xe (3rd excited state) as in part (ii) above.
- Hybridisation $= \frac{1}{2}(V + M) = \frac{1}{2}(6 + 0) = sp^3 = X$
- $\boxed{5s^2}\ \boxed{5p^1x\ \ 5p^1y\ \ 5p^1z}\ \ 5d^1xy\ \ 5d^1yz\ \ 5d^1zx$

  sp^3 hybridisation — 3 pure d-orbitals are left

No. of ($p\pi$–$p\pi$) multiple bonds = 0

No. of ($p\pi$–$d\pi$) multiple bods = 3

2.21.11 SUMMARY OF THE COMPONENT ATOMIC ORBITALS INVOLVED IN HYBRID ORBITAL FORMATION

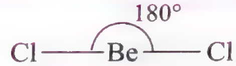
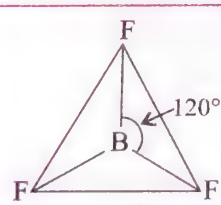
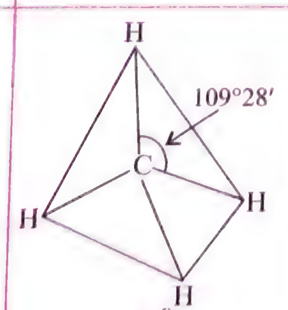
S. No.	Hybridisation	Atomic orbitals	Explanation
1.	sp, sp^2, sp^3	s + any p	—
2.	dsp^2 (OR) $dx^2-y^2\ sp^2$ (Square planar)	$dx^2-y^2+s+px+py$	This is because four lobes of dx^2-y^2 orbitals lie along x and y axes. The two p-orbitals can combine along there axes.
3.	sp^3d (OR) dsp^3 $sp^3\ dz^2$ (Tbp)	$dz^2+s+px+py+pz$ (OR) $sp^2+pz\ dz^2$	The three planar triangular hybrid orbitals are formed from one s- and two p-orbitals to form three equatorial (e) hybrid orbitals. The remaining pz orbital combines with dz^2 orbital to form two axial (a) hybrid orbitals (due to maximum overlap). The overlap of pz and dz^2 orbitals results in the formation of orbital perpendicular to triangular plane (as shown below).  Formation of sp^3d hybrid orbitals by the combination of one s and three p and $d\,(dz^2)$ orbitals.

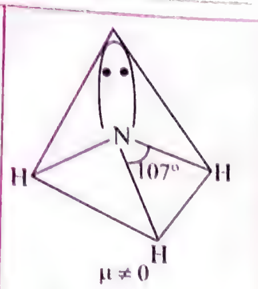
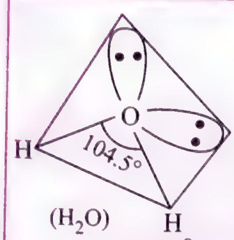
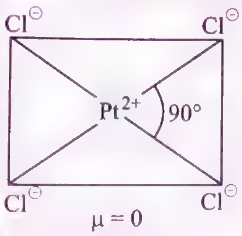
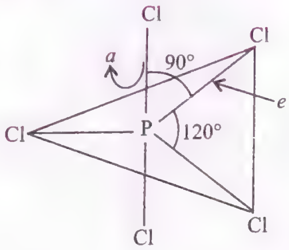
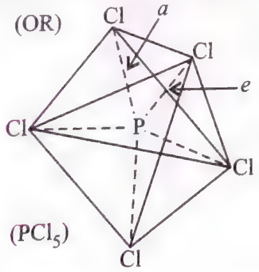
4.	sp^3d^2 (OR) d^2sp^3 or (OH)	$dx^2-y^2+dz^2+s+px+py+pz$	According to ligand field theory and advance MO theory, the *d*-orbitals which point towards the vertices of the octahedron (OH), namely dx^2-y^2 and dz^2 (i.e. along *x*, *y* and *z* axes) are used. Moreover, two *d*-orbitals required for such types of hybridisation of equal energies are only dx^2-y^2 and dz^2. Thus, these two *d*-orbitals are involved in sp^3d^2 or d^2sp^3 hybridisation.
5.	sp^3d^3 (OR) d^3sp^3 (Pbp)	$dxy+dyz+dxz+s+px+py+pz$	Three *d*-orbitals required for such type of hybridisation of equal energies are only *dxy*, *dyz* and *dxz*. Thus, these three *d*-orbitals are involved in sp^3d^3 or d^3sp^3 hybridisation.

2.21.12 Summary of Hybridisation, Geometry and Shapes of Various Molecules/Ions

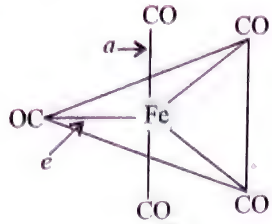
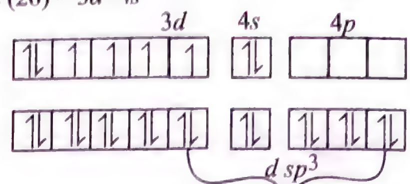
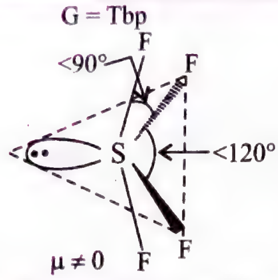
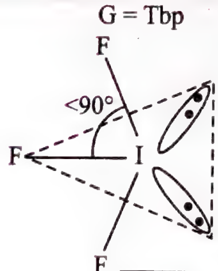
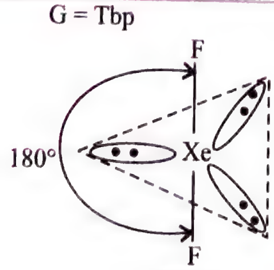
Symbols used: SN = steric number, *lp* = lone pair, *bp* = bond pair, H = hybridisation, G = geometry, S = shape, TH = tetrahedron, Tbp = trigonal bipyramid, OH = octahedral, Pbp = pentagonal bipyramid, TE = transition elements, CN = coordination number, V = no. of valence e^-'s, M = no. of monovalent attached to central atom, OS = oxidation state, (*e*) = equatorial bond, (*a*) = axial bond.

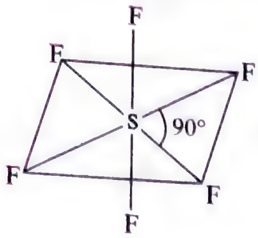
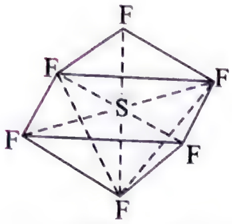
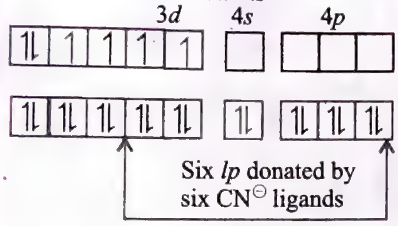
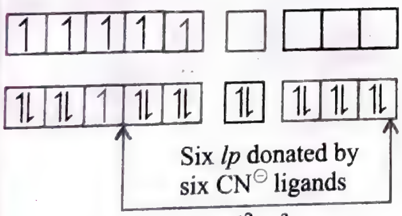
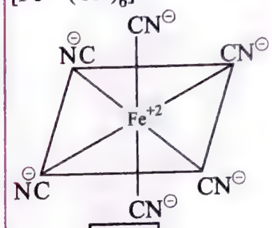
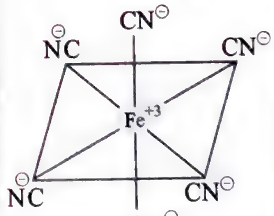
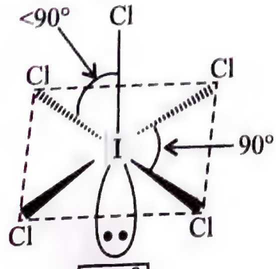
For orbital sum type: A = central atom/ion, B = atom(s) attached to central atom by covalent bond, E = lone pair of e^-'s present on central atom.

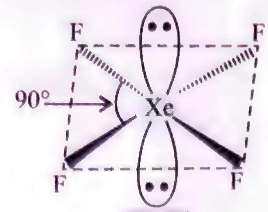
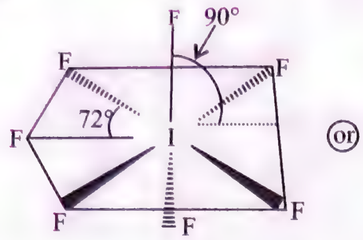
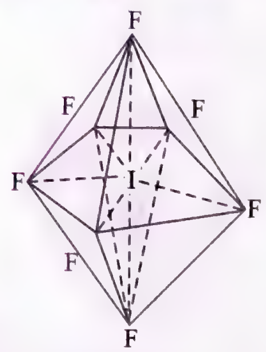
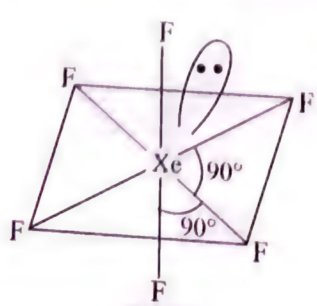
S. No.	Type of hybridisation and orbital sum		Geometry and shape and dipole moment (μ)		Angle	Example	SN = *bp* + *lp*
1.	*sp* $1+1=2$	AB	Linear	180°  $\mu = 0$ ($BeCl_2$)	180°	$BeCl_2$, $CH_2=C=CH_2$ (sp^2, sp, sp^2), $CH\equiv CH$, CO_2, $HgCl_2$, BeF_2, $ZnCl_2$, HCN, N_2, $\overset{\ominus}{C}N$	SN = 2*bp* $H=\frac{1}{2}(V+M$ $=\frac{1}{2}(2+2$ $=2$
2.a.	sp^2 $1+2=3$	AB_2	Planar or trigonal or plane triangle	 $\mu = 0$ (BF_3)	120°	$AlCl_3$, BF_3, $CH_2=CH_2$	SN = 3*bp* $H=\frac{1}{2}(V+M$ $=\frac{1}{2}(3+3$ $=3$
2.b.	sp^2 $1+2=3$	ABE	G = Planar S = Linear	$:\overset{\ominus}{C}\equiv\ddot{N}$ $\mu \neq 0$,	—	N_2, $\overset{\ominus}{C}N$	SN = 1*bp* + 1 *lp* = 2
3.a.	sp^3 $1+3=4$	AB_4	TH	 $\mu = 0$ (CH_4)	109° 28′	CH_4, SiH_4, SO_4^{2-}, PO_4^{3-}, $SnCl_4$, $ClO_4^{\ominus}$, SO_5^{2-}, $\overset{\ominus}{BF_4}$, $\overset{\oplus}{NH_4}$, PO_5^{3-}	SN = 4*bp* $H=\frac{1}{2}(V+M$ $=\frac{1}{2}(4+4$ $=4$

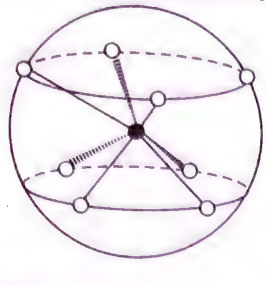
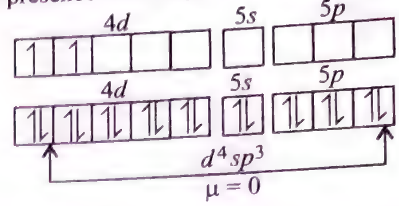
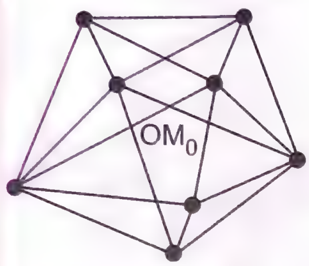
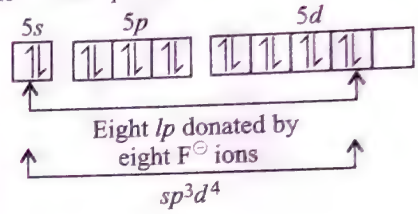
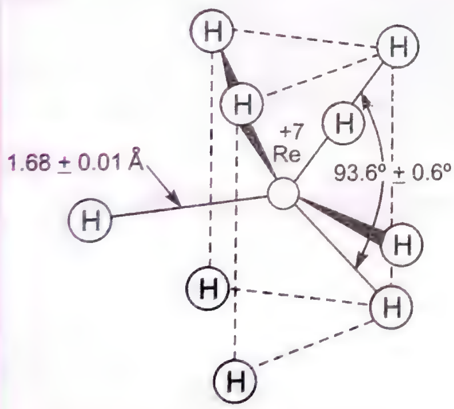
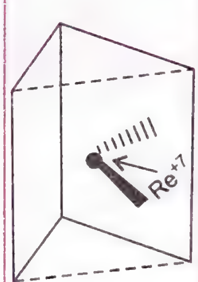
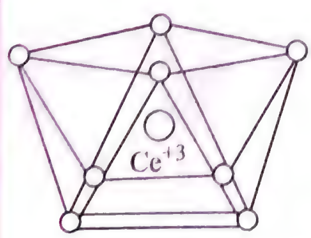
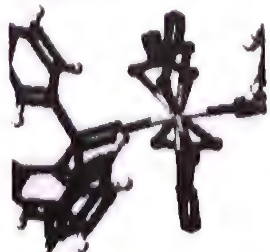
3.b.	sp^3 $1+3=4$	AB_3E	G = TH S = Pyramidal	 $\mu \neq 0$ (NH_3)	Expected angle = 109° 28′ Actual angle = 107° From VSEPR theory	$\dot{N}H_3$, $\dot{P}Cl_3$ $\dot{P}H_3$, $\dot{As}H_3$ $ClO_3^{\ominus}$, $\dot{N}F_3$	SN = 3*bp* + *lp* = 4 $H = \frac{1}{2}(V+M)$ $= \frac{1}{2}(5+3)$ $= 4$
3.c.	sp^3 $1+3=4$	AB_2E_2	G = TH S = V shape or bent or angular	 (H_2O) $\mu \neq 0$	Expected angle = 109° 28′ Actual angle = 104.5° From VSEPR theory	$H_2\ddot{O}$, $H_2\ddot{S}$:, $\ddot{P}bCl_2$, :$\ddot{O}F_2$, :$\ddot{N}H_2^{\ominus}$, :$\ddot{C}lO_2^{\ominus}$	SN = 2 *bp* + 2*lp* = 4 $H = \frac{1}{2}(V+M)$ $= \frac{1}{2}(6+2)$ $= 4$
4.	dsp^2 $1+1+2=4$ (Inner orbital complex) or low spin complex (mostly in transition elements) (Note: sp^2d is not possible)	AB_4.	G = Square planar	 $\mu = 0$	All angle 90°	$[Pt\,Cl_4]^{2-}$	SN = 4*bp* CN of Pt^{2+} is four
5.a.	sp^3d (Outer orbital complex) or high spin complex (In TE and non- TE) $1+3+1=5$ $5-2=3$ 3 means triangle and two points above and below the triangle Therefore, geometry should be trigonal bipyramid	AB_5	G = Tbp  (Due to regular geometry) ($\mu = 0$) (OR)  (PCl_5)	Three angle (ClPCl) 120° (equatorial) (*e*) and six (ClPCl) angle 90° (axial) (*a*) one angle (ClPCl) = 180° Total angle = 10	PCl_5, $SbCl_5$	SN = 5*bp* $H = \frac{1}{2}(V+M)$ $= \frac{1}{2}(5+5)$ $= 5$

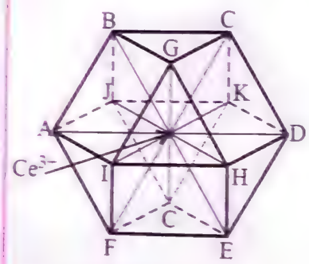
In PCl_5 there are two types of bonds. Two (P — Cl) axial bond and three (P—Cl) equatorial bond. Due to repulsion between Cl atom: (P—Cl) axial bonds are longer in bond length (240 pm) while (P—Cl) equatorial bonds are shorter in bond length (202 pm).
So, PCl_5 on heating gives $PCl_5 \rightarrow PCl_3 + Cl_2$

5.b.	dsp^3 (Inner orbital complex) (Mostly in TE) $1+1+3=5$ $5-2=3$ (explained as in 5*a*)	AB_5	G = Tbp  $\mu = 0$ (Due to regular geometry) $[Fe(CO)_5]$	Three angle 120° (*e*) and two angle 90° (*a*)	$[Fe(CO)_5]$ $Fe(26) = 3d^6\,4s^2$  Five *lp* donated by five CO molecule	SN = 5*bp* CN of Fe = 5
5.c.	sp^3d $1+3+1=5$	AB_4E	G = Tbp  (SF_4) $\mu \neq 0$ S = See-saw or Sawhorse, or folded square or (distorted/irregular) TH [**Note:** In Tbp geometry *lp's* are always placed on equatorial position for minimum repulsion and maximum stability.]	<120° and <90°		SN = 4*bp* + 1*lp* = 5 $H = \frac{1}{2}(V+M)$ $= \frac{1}{2}(6+4)$ = 5
5.d.	sp^3d $1+3+1=5$	AB_3E_2	G = Tbp  (IF_3) $\boxed{\mu \neq 0}$ S = T-shaped or arrow shapped (→)	< 90°	$:\dot{C}lF_3$, $:\ddot{I}F_3$	SN = 3*bp* + 2*lp* = 5 $H = \frac{1}{2}(V+M)$ $= \frac{1}{2}(7+3)$ = 5
5.e.	sp^3d $1+3+1=5$	AB_2E_3	G = Tbp  (XeF_2) $\boxed{\mu = 0}$ S = Linear	180°	$:\ddot{I}_3^{\ominus}$, $:\ddot{X}eF_2$	SN = 2*bp* + 3*lp* = 5 $H = \frac{1}{2}(V+M)$ $= \frac{1}{2}(8+2)$ = 5

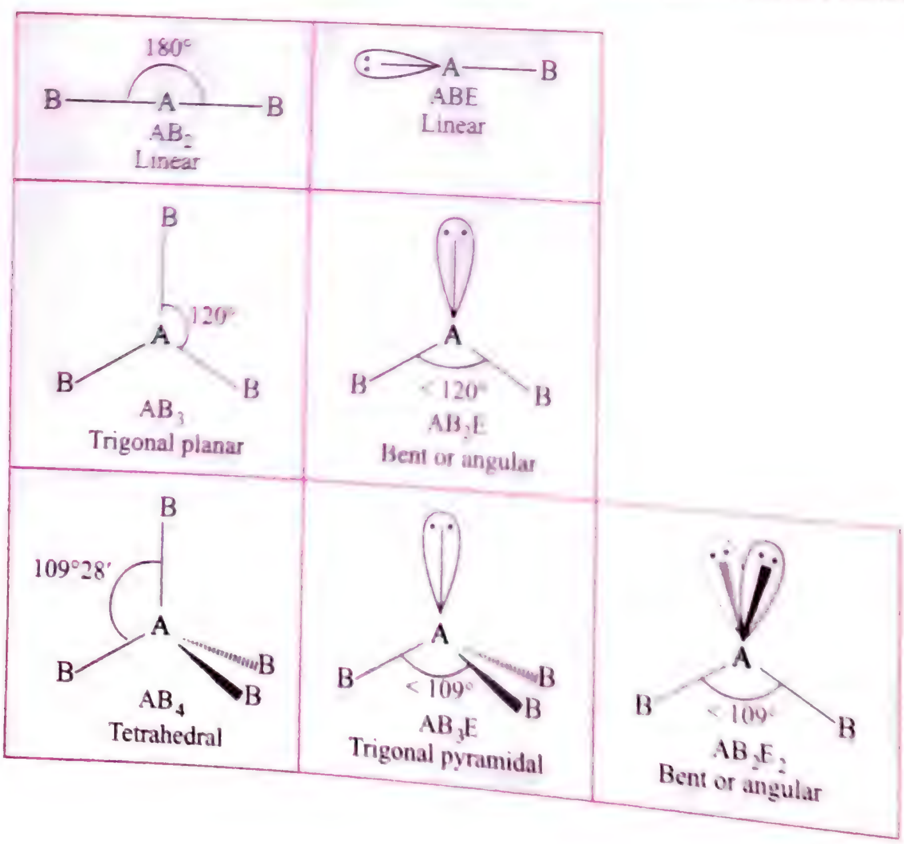
6.a.	sp^3d^2 (Outer orbital complex) (In TE and non-TE) $1+3+2=6$ $6-2=4$ 4 means. square and two points above and below the square. Therefore, geometry should be square bipyramid but it is called octahedral	AB_6	OH  (OR)  (SF_6) $\mu = 0$ (Regular geometry)	All angle 90°	SF_6, $PF_6^{\ominus}$, $SnCl_6^{\ominus}$	SN = 6*bp* $H = \frac{1}{2}(V+M)$ $= \frac{1}{2}(6+6)$ $= 6$
6.b.	d^2sp^3 (Inner orbital complex) (Mostly in TE) $2+1+3=6$ $6-2=4$ (explained as in 6a)	AB_6	OH Fe (26) = $3d^6\,4s^2$ $Fe^{2+} = 3d^6\,4s^0$  Therefore, in $[Fe^{2+}(CN)_6]^{4-}$, no unpaired e^- and the compound is diamagnetic and colourless. In $[Fe^{3+}(CN)_6]^{3-}$ Fe(26) = $3d^6\,4s^2$ $Fe^{+3} = 3d^5\,4s^0$  In $[Fe(CN)_6]^{3-}$, there is one unpaired e^- and the compound is paramagnetic and coloured. $\mu_{MM} = \sqrt{n(n+2)}$ BM (n = no. of unpaired e^-) $= \sqrt{3}$ BM	All angles 90°	$[Fe^{2+}(CN)_6]^{4-}$ (or) $[Fe^{3+}(CN)_6]^{3-}$  $\boxed{\mu = 0}$  $\boxed{\mu = 0}$	SN = 6*lp* CN of $Fe^{2+} = 6$ CN of $Fe^{3+} = 6$
6.c.	sp^3d^2 $1+3+2=6$	AB_5E	G = OH  (ICl_5) $\boxed{\mu \neq 0}$ S = Square pyramidal	90° (e) and < 90° (a)	$\ddot{I}Cl_5$, $\ddot{Br}F_5$, $\ddot{I}F_5$, $:XeOF_4$	SN = 5*bp* + 1*lp* $= 6$ $H = \frac{1}{2}(V+M)$ $= \frac{1}{2}(7+5)$ $= 6$

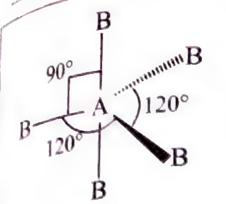
6.d.	sp^3d^2 $1 + 3 + 2 = 6$	AB_4E_2	G = OH  (XeF_4) $\boxed{\mu = 0}$ S = Square planar	90°	$:\ddot{X}eF_4$, $ICl_4^{\ominus}$	$SN = 4bp + 2lp$ $= 6$ $H = \frac{1}{2}(V + M)$ $= \frac{1}{2}(8 + 4)$ $= 6$
7.a.	sp^3d^3 (Outer orbital complex) (In TE and non-TE) $1 + 3 + 3 = 7$ $7 - 2 = 5$ 5 means pentagonal and two points above and below pentagon. Therefore, geometry is pentagonal bipyramid.	AB_7	Pbp  (or)  (IF_7) $\mu = 0$ (Regular geometry)	Five angles of 72° (e) and two angles of 90° (a)	IF_7 (Inter-halogen compound)	$SN = 7bp$ $H = \frac{1}{2}(V + M)$ $= \frac{1}{2}(7 + 7)$ $= 7$
	In IF_7 there are two types of bonds. Two (I – F) axial bond and 5 (I – F) equatorial bond. Five (I – F) bonds are at 72° and have more repulsion than two (I – F) bonds which are at 90°. Thus, five (I – F) equatorial bonds are longer in bond length and are weaker, thus on heating five (I – F) equatorial bond breaks. Hence, IF_7 on heating gives $IF_2 + \frac{5}{2}F_2$.					
7.b.	d^3sp^3 (Inner orbital complex) (Mostly in TE) $1 + 3 + 3 = 7$ $7 - 2 = 5$ (explained as in 7a)	AB_7	Pentagonal bipyramid	Five angles of 72° and two angles of 90°.		
7.c.	sp^3d^3 $1 + 3 + 3 = 7$	AB_6E	G = Pbp Shape = It should be pentagonal pyramid but it is a distorted OH or monocapped OH.  $\boxed{\mu \neq 0}$	90° (e) and 90° (a)	$\ddot{X}eF_6$	$SN = 6bp + 1lp$ $= 7$ $H = \frac{1}{2}(V + M)$ $= \frac{1}{2}(8 + 6)$ $= 7$

8.a.	d^4sp^3 Inner orbital complex. Such type of hybridisation occurs only in lanthanides and actinides elements. Lignand should be of small size having high EN. Metal must be in higher OS. $4+1+3=8$	Shape: Cube or square antiprism or hexagonal bipyramid or dodecahedron or Archimedes antiprism  Square antiprism	$[Mo^{4+}(CN)_8]^{4-}$ Mo (Z = 42) $4d^5\ 5s^1$ $Mo^{4+} = 4d^2\ 5s^0\ 5p^0$ In presence of strong $CN^{\ominus}$ ligand, 	CN = 8
8.b.	sp^3d^4 $1+3+4=8$	For $[Mo(CN)_8]^{4-}$ $\bullet \Rightarrow Mo^{+4}$ $o \Rightarrow 8\ CN^{\ominus}$ ions For $[XeF_8]^{2-}$, $\bullet \Rightarrow Xe^{+6}$ $o \Rightarrow 8F^{\ominus}$ ions 	$[Xe^{+6}F_8]^{2-}$ $Xe = 5s^2\ 5p^6\ 5d^0$ $Xe^{+6} = 5s^0\ 5p^0\ 5d^0$ 	CN = 8
9.	d^5sp^3 All hydrated salts of lanthanides show this type of hybridisation $5+1+3=9$	Three-face centred trigonal prism (or) capped trigonal prism  	$[Eu^{3+}(H_2O)_9]^{3+}$ and $\left[\overset{+7}{Re}\ \overset{-1\times 9}{Ha}\right]^{2-}$	CN = 9
10.	Hybridisation is not mentioned. But compounds with CN = 10 are given.	Bicapped square antiprism  CN = 10 Bicapped square antiprism (D4d) Tetrakis(nitrato-O,O') -bis (triphenylphosphin) 	$[Ce^{3+}(NO_3)_5]^{2-}$ **Note:** $NO_3^{\ominus}$ acts here bidentate ligand. Hence CN = 2 × 5 = 10	

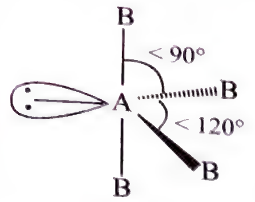
11.	Hybridisation is not mentioned. But compounds with CN = 11 are given, but generally not very common	**CN = 11** All-faced capped trigonal prism (D3h) This is not a common stereochemistry In aqua-(12-crown-4)-tris(nitrato-O,O')-cer solvate and (15-crown-5)-tris (nitrato-O,O') ion is 11 coordinate 	
12.	Hybridisation is not mentioned. But compounds with CN = 12 are given.	CN = 12 cuboctahedron (Oh) Ceric ammonium nitrate-$(NH_4)_2[Ce(NO_3)_6]$  	$\overset{+1}{(NH_4)_2}[Ce^{3+}\overset{-1}{(NO_3)_6}]$ **Note:** NO_3^- acts here bidetate ligand. ∴ CN = 2 × 6 = 12

2.21.13 Summary of Possible Shapes of Molecules/Ions and f-Orbitals

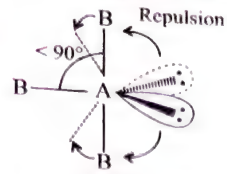




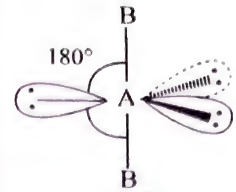
AB_5
Trigonal bipyramidal



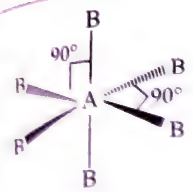
AB_4E
Sawhorse or see-saw



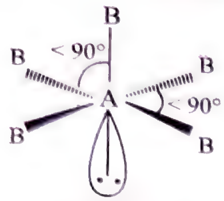
AB_3E_2
T-shape or
(arrow shape)



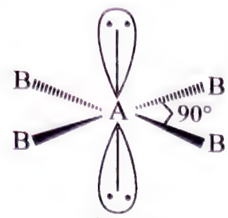
AB_2E_3
Linear



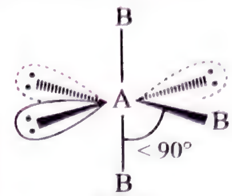
AB_6
Octahedral



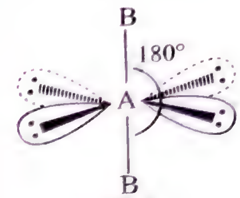
AB_5E
Square pyramidal



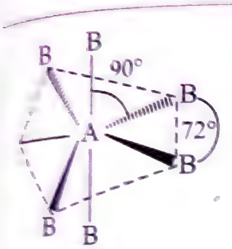
AB_4E_2
Square planar



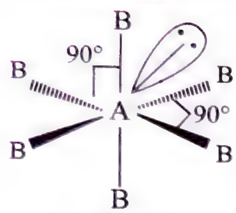
AB_3E_3
T-shape



AB_2E_4
Linear

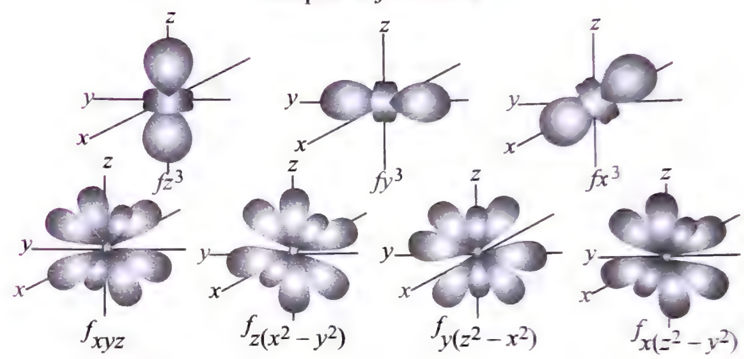


AB_7
Pentagonal
bipyramidal



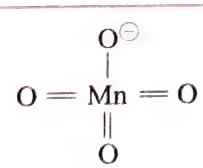
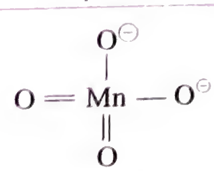
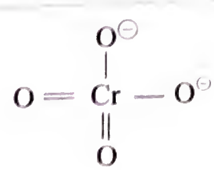
AB_6E
Distorted OH or
monocapped OH

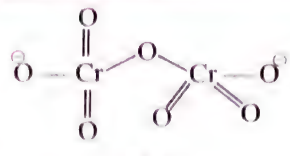
Shapes of *f*-orbitals



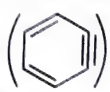
2.21.13.1 Some Other Examples

Symbols used: SN = steric number, *lp* = lone pair, *bp* = bond pair, H = hybridisation, G = geometry, S = shape, TH = tetrahedron, Tbp = trigonal bipyramid, OH = octahedral, Pbp = pentagonal bipyramid, TE = transition elements, CN = coordination number, V = no. of valence e^-'s, *M* = no. of monovalent attached to central atom, OS = oxidation state, (*e*) = equatorial bond, (*a*) = axial bond

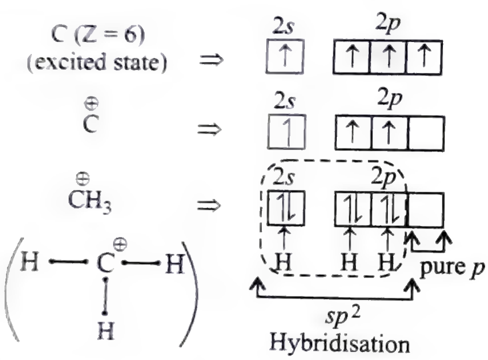
1.	$MnO_4^{\ominus}$	(Permanganate ion)	 $\mu = 0$	SN = 4*bp*	H = sp^3	G = TH
2.	MnO_4^{2-}	(Manganate ion)	 $\mu = 0$	SN = 4*bp*	H = sp^3	G = TH
3.	CrO_4^{2-}	(Chromate ion)	 $\mu = 0$	SN = 4*bp*	H = sp^3	G = TH

4.	$Cr_2O_7^{2-}$	(Dichromate ion)	 $\mu = 0$	SN= $4bp$	H = sp^3	G = TH

2.21.14 Hybridisation of Reactive Intermediates

There are various reactive intermediates which are produced in situ (i.e. inside the reaction) during organic reactions. These are (i) Carbocation ($\overset{\oplus}{C}H_3$), (ii) Carbanion ($\overset{\ominus}{C}H_3$), (iii) Free radical ($\dot{C}H_3$), (iv) Carbene ($\cdot CH_2 \cdot$), (v) Radical cation ($\cdot\overset{\oplus}{C}H_2$), (vi) Nitrene ($R - \ddot{N}:$) and (vii) Benzyne .

1. Hybridisation of carbocation ($\overset{\oplus}{C}H_3$):



a. SN = $3bp = 3 = sp^2$

b. $H = \frac{1}{2}[(V + M - (+\text{ve charge})]$

$= \frac{1}{2}(4 + 3 - 1) = 3 = sp^2$

c. G = Planar, Bond angle ≈ 120°

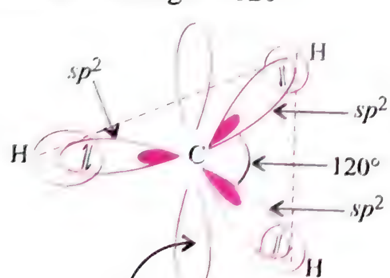
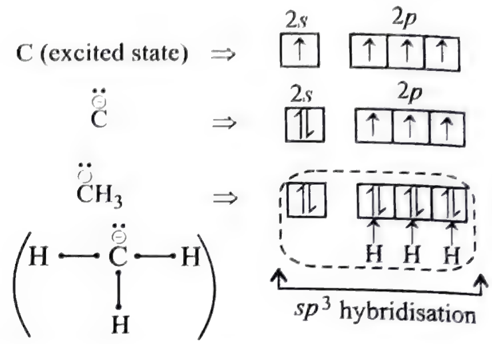


Fig. 2.42 Formation of $\overset{\oplus}{C}H_3$

[3σ (C — H) bonds are formed by overlap of sp^2 (C) with 1s (H)]

Note: Hybrid orbital can be represented either by () or by ().

2. Hybridisation of carbanion ($\ominus\ddot{C}H_3$):



a. SN = 3 bp + 1lp = 4 = sp^3

b. $H = \frac{1}{2}[(V + M + (-\text{ve charge})]$

$= \frac{1}{2}(4 + 3 + 1) = 4 = sp^3$

c. G = TH, Shape = Pyramidal. Bond angle < 109° (due to lp–bp and bp–bp repulsions)

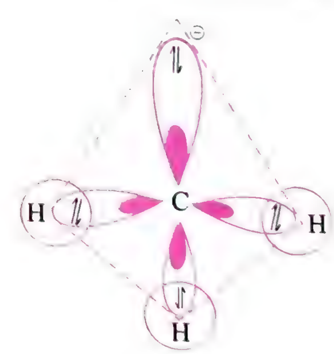
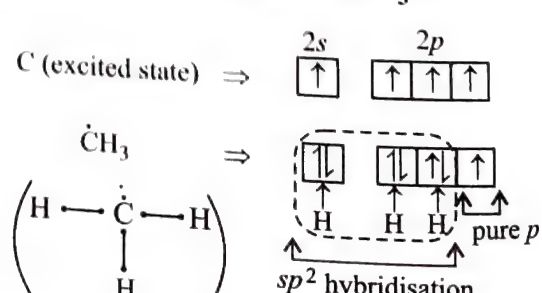


Fig. 2.43 Formation of $\overset{\ominus}{C}H_3$

[Three σ (C – H) bonds are formed by overlap of sp^3 (C) – 1s (H) one lp with –ve charge is present in vacant sp^3 hybrid orbital]

3. Hybridisation of free radical ($\dot{C}H_3$):



a. $SN = 3bp = 3 = sp^2$

b. $H = \frac{1}{2}(V + M)$ rule is not applicable in this case.

c. G = Planar, Bond angle < 120°

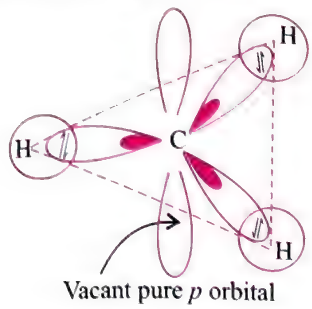


Fig. 2.44 Formation of $\dot{C}H_3$

[Three σ (C – H) bonds are formed by overlap of sp^3 (C) – 1s (H)]

4. **Hybridisation of carbene ($\cdot CH_2 \cdot$):** Carbenes are neutral species which has divalent C atom having two unshared electrons (or two odd electrons). In carbene, C atom has six electrons in the outer shell. Therefore, carbenes are electron deficient in nature. Carbenes are of two types: (a) Singlet and (b) Triplet.

a. **Singlet carbene:** The singlet carbene has two unshared electrons with opposite spins paired in one sp^2 hybrid orbital, e.g.

$$\begin{bmatrix} (\uparrow \cdot CH_2 \cdot \downarrow) \\ +\frac{1}{2} \quad -\frac{1}{2} \end{bmatrix}$$

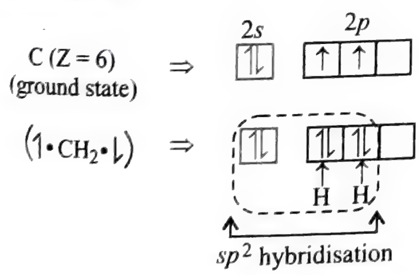
They are called singlet because their spin state is one.

$\therefore$ Spin number (S) $= +\frac{1}{2} - \frac{1}{2} = 0$

Since there are no unpaired e^-'s.

$\therefore$ Spin state = (2S + 1) = (2 × 0 + 1) = 1

Hybridisation:



Since two odd e^-'s are of opposite spins, therefore they are considered as one lp. They use sp^2 hybrid orbital in bond formation with bent shape.

i. $SN = 2bp + 1lp = 3 = sp^2$

ii. $H = \frac{1}{2}(V + M) = \frac{1}{2}(4 + 2) = 3 = sp^2$

iii. G = Planar

iv. Shape = Bent

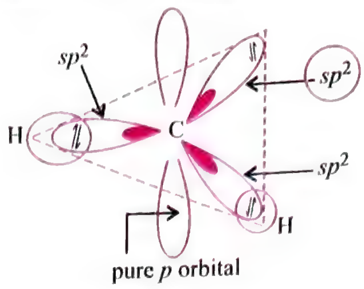


Fig. 2.45 Formation of singlet carbene

- Two σ (C – H) bonds are formed by overlap of sp^2 (C) with 1 s (H).
- Two e^-'s are present in one sp^2 hybrid orbital marked as sp^2 (circled).
- Bond angle (H – C – H) = 103° and bond length (C – H) = 112 pm.

b. Triplet carbene: The triplet carbene has two electrons with the same spin, each in a different orbital making it a diradical, e.g. $\begin{bmatrix} (\uparrow \cdot CH_2 \cdot \uparrow) \\ +\frac{1}{2} \quad +\frac{1}{2} \end{bmatrix}$.

They are called triplet because their spin state is 3.

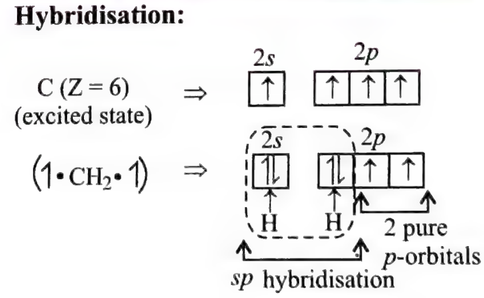
$\therefore$ Spin number (S) $= \left(+\frac{1}{2} + \frac{1}{2}\right) = 1.$

Since there are two unpaired e^-'s with same spin,

$\therefore$ Spin state = (2S + 1) = (2 × 1 + 1) = 3

Note: Two e^-'s with same spin are not considered as one lp.

Hybridisation:



They use sp hybrid orbital in bond formation, with linear shape. They show bond angle (H – C – H) of 180° and bond length (C – H) of 103 pm.

i. $SN = 2bp = 2 = sp$

ii. $H = \frac{1}{2}(V + M)$ is not applicable

iii. G = Linear, Bond angle = 180°

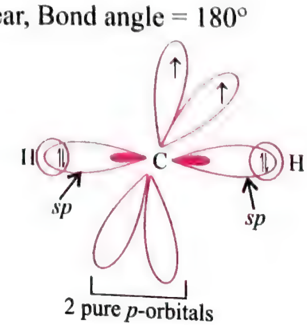
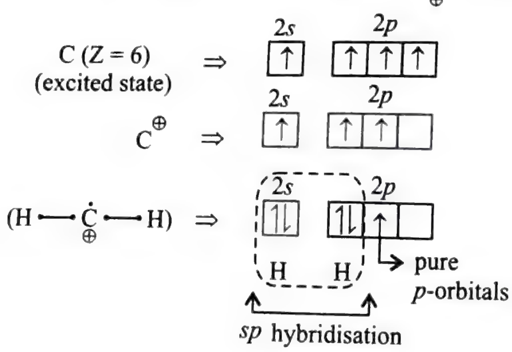


Fig. 2.46 Formation of triplet carbene

- Two σ (C – H) bonds are formed by the overlap of sp(C) with $1s$(H).
- Two e^-'s are present in two pure p-orbitals making it a diradical.

5. Hybridisation of radical cation $(H—\dot{C}^{\oplus}—H)$:



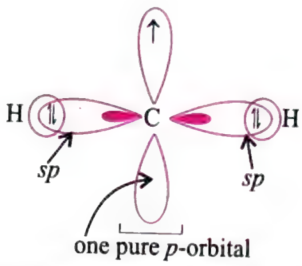


Fig. 2.47 Formation of radical cation

a. SN = 2bp = 2 = sp

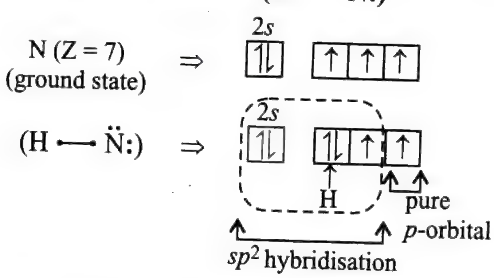
b. $H = \frac{1}{2}(V + M)$ is not applicable in this case

c. G = Linear, Bond angle = 180°

i. Two σ (C – H) bonds are formed by the overlap of sp (C) with $1s$ (H).

ii. One electron is present in pure $2p$-orbital.

6. Hybridisation of nitrene $(H—\ddot{N}:)$



a. $SN = 1\ bp + 2\ lp = 3 = sp^2$

b. $H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 1) = 3 = sp^2$

c. G = Planar

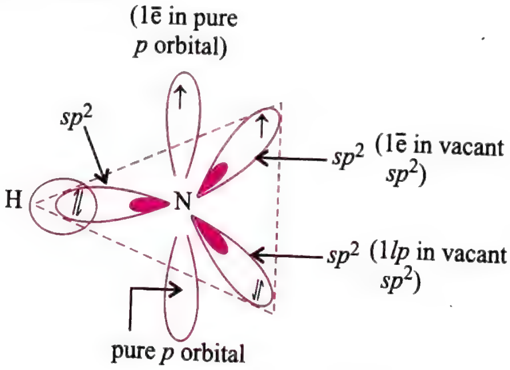


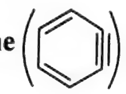
Fig. 2.48 Formation of nitrene

i. One σ (N – H) bond is formed by the overlap of sp^2 (N) with $1s$ (H).

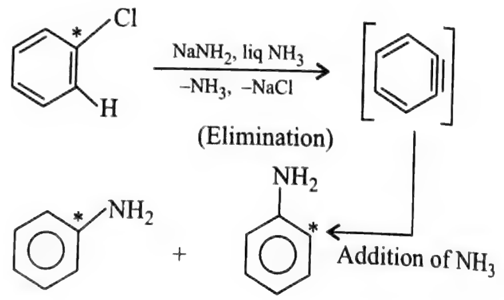
ii. One lp is present in vacant sp^2 hybrid orbital.

iii. One e^- is present in vacant sp^2 orbital.

iv. One e^- is present in vacant pure p-orbital.

7. Hybridisation of benzyne  **:**

Benzyne is a reactive intermediate in aromatic nucleophilic substitution (ArSN) reaction, i.e. elimination addition reaction, e.g.



Benzyne may be regarded as benzene with 2H atoms removed.

Benzyne has additional π-bond formed by the sideway overlap of sp^2 hybrid orbitals alongside the ring (i.e. belonging to two neighbouring C atoms). These orbitals that form π-bond cannot overlap with the aromatic π-system, because they are not coplanar. The new π-bond is a weak bond because of poor overlap and hence benzyne is very reactive.

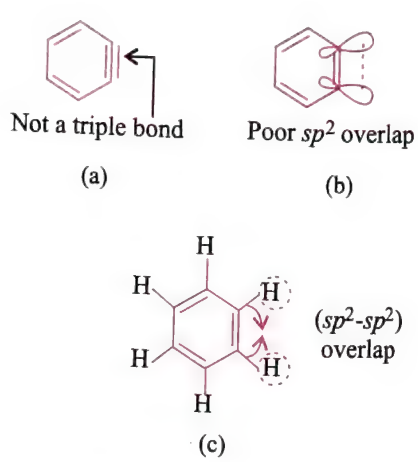
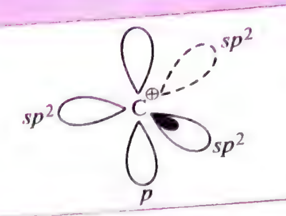
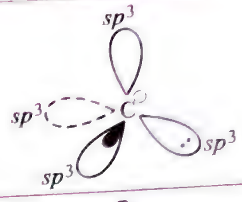
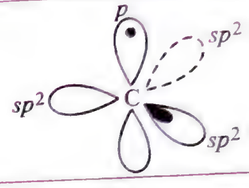
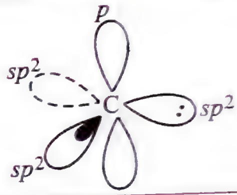
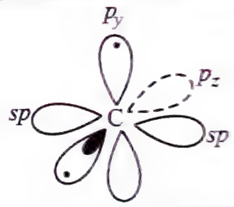
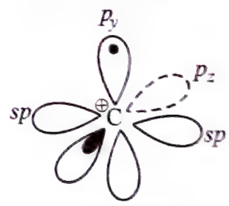


Fig. 2.49 Structure of benzyne

Table 2.13 Summary of various reactive intermediates

S.No.	Intermediate species	FC (formal charge)	Steric number (lp + bp)	Hybridisation and shape	Wedge formula	Orbital representation
1.	Carbocation $H-\overset{\oplus}{C}-H$ with H below	$4-0-\frac{1}{2}(6)$ $=+1$	$3+0=3$	sp^2 planar		
2.	Carbanion $H-\overset{\ominus}{\ddot{C}}-H$ with H below	$4-2-\frac{1}{2}(6)$ $=-1$	$3+1=4$	sp^3 pyramidal		
3.	Free radical $H-\dot{C}-H$ with H below	$4-1-\frac{1}{2}(6)$ $=0$	$3+0=3$	sp^2 planar		
4.	Singlet carbene $H-C:$ with H below	$\left[4-2-\frac{1}{2}(4)\right]$ $=0$	$2+1=3$	sp^2 bent		
5.	Triplet carbene $H-\dot{\underset{\cdot}{C}}-H$	$4-1-\frac{1}{2}(4)$ $=0$	$2+0=2$	sp linear		
6.	Radical cation $H-\underset{\oplus}{\dot{C}}-H$	$4-1=\frac{1}{2}(4)$ $=+1$	$2+0=2$	sp linear		
7.	Nitrene $H-\ddot{N}:$	$5-4-\frac{1}{2}(2)=0$	$2+1=3$	sp^2		

2.21.15 Exceptional Case of Hybridisation in Trisilyl Amine $N(SiH_3)_3$ and Diborane (B_2H_6)

Hybridisation in $N(SiH_3)_3$: The hybridisation around N-atom in trimethyl amine $N(CH_3)_3$ is sp^3 with pyramidal geometry as expected. Whereas in case of trisilyl amine the hybridisation and geometry should be sp^3 and pyramidal as in $N(CH_3)_3$ but the hybridisation and geometry are observed as sp^2 and planar respectively. This can be explained due to ($p\pi$–$d\pi$) multiple or back bonding as shown:

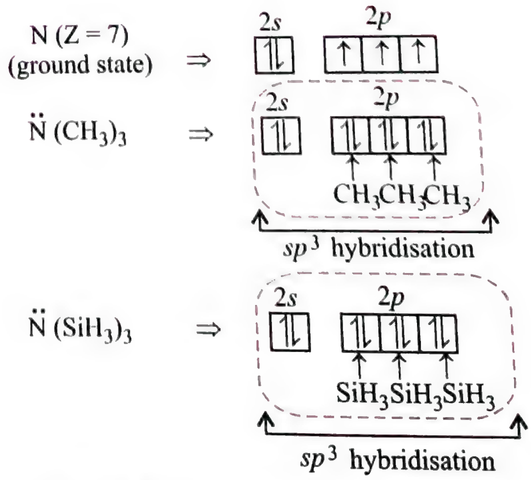
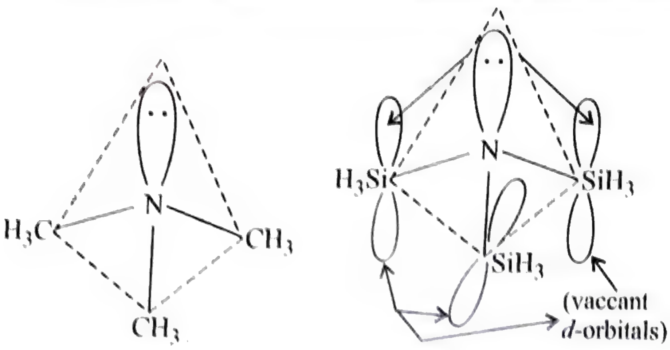
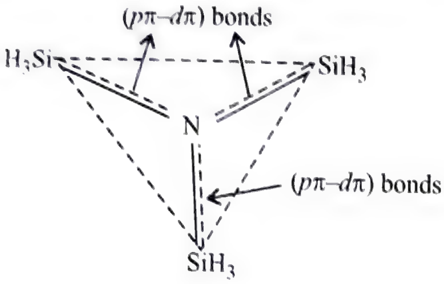


Fig. 2.50. Structures of $N(CH_3)_3$ and $N(SiH_3)_3$



G = TH Expected G = TH

Shape = Pyramidal Expected shape = Pyramidal



Observed G = Planar

[Due to ($p\pi$–$d\pi$) multiple or back bonding]

Hybridisation in B_2H_6:

B (Z = 5) (ground state) $2s$ [↑↓] $2p$ [↑| |]

B (excited state) $2s$ [↑] $2p$ [↑|↑|]

1. Structure of diborane: The four-terminal H atoms and two B atoms lie in one plane. There are two bridging H atoms. The four-terminal (B–H) bonds are regular ($2c$, $2e^-$) bonds as shown in Fig. 2.51.

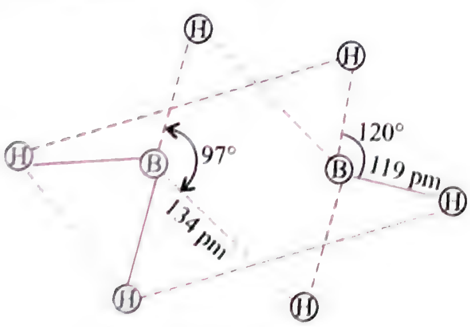
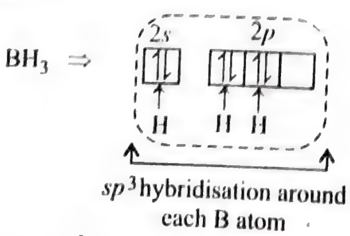


Fig. 2.51 Structure of B_2H_6

2. Hybridisation:



Each B atom uses sp^3 hybrid orbitals for bonding. Out of the four hybrid orbitals each B atom is without an electron as shown in broken lines in Fig. 2.52. The terminal B–H bonds are normal ($2c$, $2e^-$) bonds but the two bridge bonds are ($3c$, $2e^-$) bonds, and are also referred to as banana bonds or Tau bonds or bridge bonds.

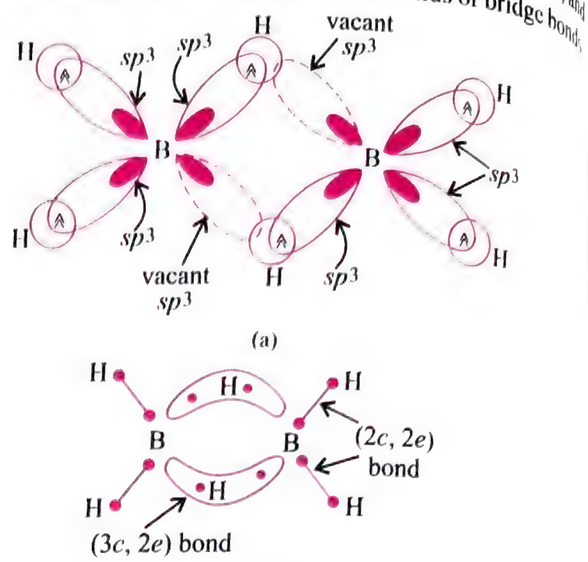


Fig. 2.52 Hybridisation in B_2H_6

a. Two (B – H – B) bridge bonds are formed by the overlap of both filled sp^3 (B) and vacant sp^3 (B) with $1s$ (H).

b. Four σ (B – H) bonds are formed by the overlap of filled sp^3 (B) with $1s$ (H).

Note: This is the special case in which vacant p-orbital also takes part in hybridisation.

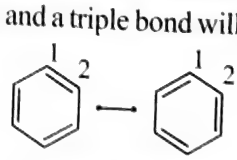
2.22 CALCULATION OF BOND ORDER FOR MOLECULES SHOWING RESONANCE

1. Molecules or ions having resonance: The bond order is calculated as follows:

$$\text{Bond order} = \frac{\text{Total no. of bonds between two atoms in all the structures}}{\text{Total no. of resonating structures}}$$

(Any two bonded atoms may be selected and a double bond will mean two bonds and a triple bond will mean three bonds) e.g.

a. In benzene:

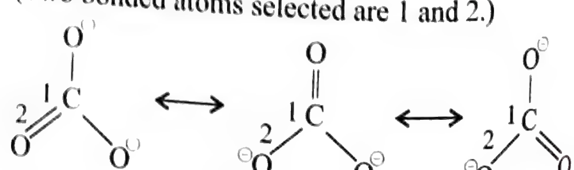


[Two bonded atoms selected are 1 and 2]

$$\text{Bond order} = \frac{\text{Double bond + Single bond}}{2} = \frac{2+1}{2} = 1.5$$

b. In carbonate ion:

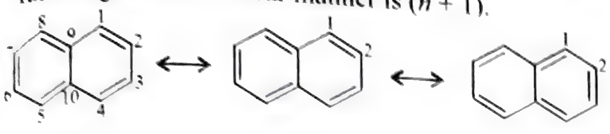
(Two bonded atoms selected are 1 and 2.)



$$\text{Bond order} = \frac{\text{Double bond + Single bond + Single bond}}{3}$$

$$= \frac{2+1+1}{3} = 1.33$$

c. In naphthalene: The number of resonating structures for polynuclear hydrocarbons containing n benzene rings fused together in a linear manner is $(n + 1)$.



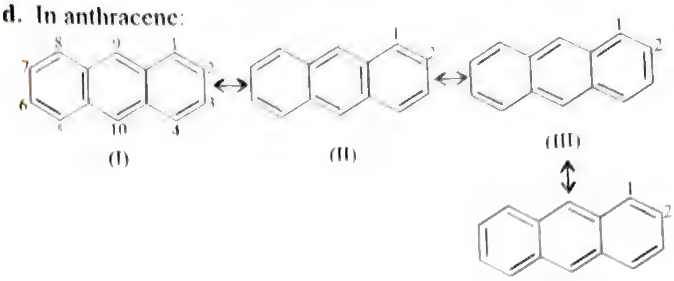
(I) (II) (III)

(Two bonded atoms selected are 1 and 2.)

$$\text{Bond order} = \frac{\text{Double bond in (I)} + \text{Double bond in (II)} + \text{Single bond in (III)}}{\text{Total resonating structure}}$$

$$= \frac{2+2+1}{3} = \frac{5}{3} = 1.66$$

d. In anthracene:



(I) (II) (III) (IV)

(Two bonded atoms selected are 1 and 2.)

$$\text{Bond order} = \frac{\text{Double bond in (I)} + \text{Double bond in (II)} + \text{Single bond in (III)} + \text{Double bond in (IV)}}{\text{Total resonating structures}}$$

$$= \frac{2+2+1+2}{4} = \frac{7}{4} = 1.75$$

2. **Shapes and bond order of isoelectronic species:** Isoelectronic species have the same shape and same bond order, e.g. see Table 2.14.

Table 2.14 Bond order and shape of some molecules/ions

S.No.	Species	Structures (Note: Two bonded atoms selected are shown by 1 and 2)	No. of valence electrons	Shape	Bond order
1.	CO_2	$O = C^1 = O^2$ Bond order $= \frac{2}{1} = 2$	$4 + 2 \times 6 = 16$	Linear	2
2.	$N_3^{\ominus}$ (Azide ion)	$[:\ddot{N} = N_1 = \ddot{N}_2:]^{\ominus} \leftrightarrow [:\ddot{N} - N_1 \equiv N_2:]^{\ominus} \leftrightarrow [N \equiv N_1 - \ddot{N}_2:]^{\ominus}$ I II III Bond order $= \frac{2+3+1}{3} = 2$	$3 \times 5 + 1 = 16$	Linear	2
3.	$NO_2^{\ominus}$ (Nitrite ion)	$[\ddot{O} = \ddot{N}^1 - \ddot{O}^2:]^{\ominus} \leftrightarrow [:\ddot{O} - \ddot{N}^1 = \ddot{O}^2]^{\ominus}$ I II Bond order $= \frac{1+2}{2} = 1.5$	$5 + 2 \times 6 + 1 = 18$	V-shaped	1.5
4.	O_3	$[:\ddot{O} = \dot{O}^1_{\oplus} - \ddot{O}^{2\ominus}:] \leftrightarrow [:\ddot{O}^{\ominus} - \dot{O}^1_{\oplus} = \ddot{O}^2]$ I II Bond order $= \frac{1+2}{2} = 1.5$	$3 \times 6 = 18$	V-shaped	1.5
5.	$NO_3^{\ominus}$ (Nitrate ion)	$[:\ddot{O} = N^1(-\ddot{O}:) - \ddot{O}^2:]^{\ominus} \leftrightarrow [:\ddot{O} - N^1(-\ddot{O}:) = \ddot{O}^2:]^{\ominus} \leftrightarrow [:\ddot{O} - N^1(=\ddot{O}:) - \ddot{O}^2:]^{\ominus}$ I II III Bond order $= \frac{1+2+1}{3} = 1.33$	$5 + 6 \times 3 + 1 = 24$	Plane triangular	1.33
6.	CO_3^{2-}	$[:\ddot{O} = C^1(-\ddot{O}:) - \ddot{O}^2:]^{2-} \leftrightarrow [:\ddot{O} - C^1(-\ddot{O}:) = \ddot{O}^2:]^{2-} \leftrightarrow [:\ddot{O} - C^1(=\ddot{O}:) - \ddot{O}^2:]^{2-}$ I II III Bond order $= \frac{1+2+1}{3} = 1.33$	$4 + 3 \times 6 + 2 = 24$	Plane triangular	1.33

3. a. Relation between hybridisation and bond angle and percent of *s*-character: The relation between hybridisation and bond angle is simple for *s–p* hybrids. For two or more equivalent orbitals, the per cent of *s*-character or the per cent of *p* character is given by the relationship.

$$\cos\theta = \frac{s\%}{s\% - 100} = \frac{p\% - 100}{p\%}$$

where θ is the angle between the equivalent orbitals (°).

For example, in methane (CH_4) (sp^3 hybridisation)

% of *s*-character = 25%

% of *p*-character = 75%

$$\therefore \cos\theta = \frac{25}{25-100} = \frac{25}{-75} = -0.333;\ \theta = 109.5^\circ$$

or $$\cos\theta = \frac{75-100}{75} = \frac{-25}{75} = -0.333;\ \theta = 109.5^\circ$$

b. Calculation of per cent of *s*-character: The number of *p*-orbitals that takes in hybridisation is called the hybridisation index (*m*). For organic molecules,

$$\cos\theta = -\frac{1}{m}$$

where θ is the bond angle between the two hybrid orbitals, e.g. for *sp* hybridisation, $m = 1$ ($\because p = 1$). Hence, $\cos\theta = -1$ or $\theta = 180^\circ$. For sp^2 hybridisation, $m = 2$. ($\because p = 2$). Hence, $\cos\theta = -1/2$ or $\theta = 120^\circ$.

Knowing the angle between the hybrid orbitals, *m* can be calculated. Then

$$\%\text{ of } s\text{-character} = \frac{1}{1+m} \times 100$$

ILLUSTRATION 2.21

Explain the hybridisation of carbon atoms in allene (C_3H_4) and show the *p*-orbital overlaps.

Sol. Allene is $\overset{1}{C}H_2 = \overset{2}{C} = \overset{3}{C}H_2$. Carbon atoms 1 and 3 are in sp^2 hybridised state while carbon 2 is in *sp* hybridised state. Two unhybridised orbitals of carbon 2 overlap sidewise to form π-bonds besides it also forms a sigma bond with each of the carbon atoms using hybridised orbitals. Two hybridised orbitals of each of carbon 1 and 2 form sigma bonds with hydrogen atoms.

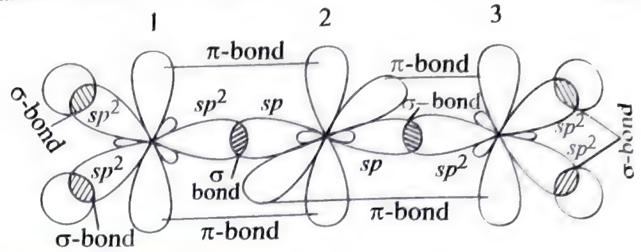


ILLUSTRATION 2.22

Out of the following species, group them having similar structures:

CH_4, CO_3^{2-}, CO_2, $\overset{\oplus}{N}H_4$, $NO_3^{\ominus}$, $N_3^{\ominus}$, $BF_4^{\ominus}$, SO_2, $NO_2^{\ominus}$.

Sol. Isoelectronic species with same no. of e^-'s usually have the same structure. This may be extended to species with the same number of valence electrons on the central atom.

	Species	Structures and hybridisation	No. of e^-'s
1.	CH_4, $\overset{\oplus}{N}H_4$, $BF_4^{\ominus}$	Tetrahedral, sp^3	10
2.	CO_3^{2-}, $NO_3^{\ominus}$, SO_2,	Plane triangle, sp^2	32
3.	CO_2, $N_3^{\ominus}$, $NO_2^{\oplus}$	Linear, *sp*	22

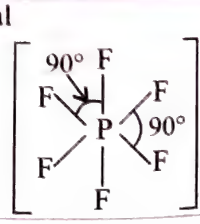
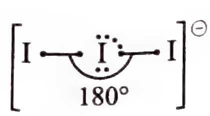
ILLUSTRATION 2.23

Determine the hybridisation, geometry, number of lone pairs (*lp*'s) and bond pairs (*bp*'s) excluding π bonds in the following compounds.

a. $PF_6^{\ominus}$ b. $I_3^{\ominus}$ c. ClF_3 d. $XeOF_4$

e. SO_2 f. SO_3 g. $IF_4^{\oplus}$ h. $\overset{\oplus}{N}H_4$

Sol.

S.No.	Compound	Hybridisation *lp* and *bp*'s	Geometry	Shape
a.	$PF_6^{\ominus}$	$H = \frac{1}{2}(V + M + 1) = \frac{1}{2}(5 + 6 + 1) + 6$ $H = sp^3d^2$ *lp* at P atom = 0, *bp* at P atom = 6	Octahedral	Octahedral 
b.	 ($I_3^{\ominus}$)	$H = \frac{1}{2}(V + M + 1) = \frac{1}{2}(5 + 6 + 1)$ $H = sp^3d^2$ *lp* at each I atom = 3 *bp* at central I atom = 2	Trigonal bipyramid	Linear 

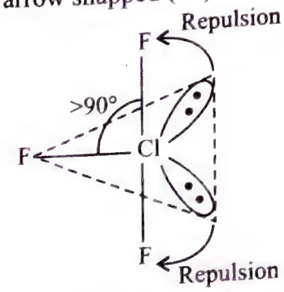
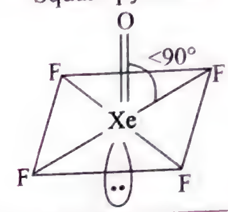
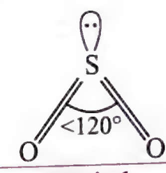
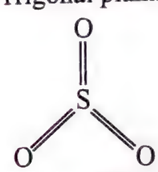
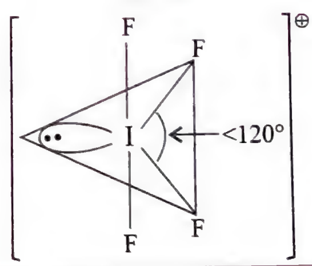
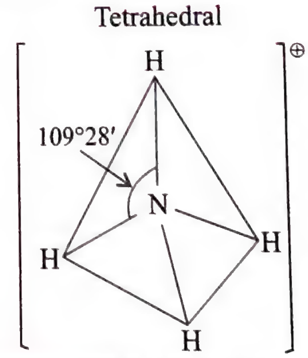
c.	$:\ddot{C}lF_3$	$H = \frac{1}{2}(7+3) = 5$ $H = sp^3d$ *lp* at Cl atom = 2 *bp* at Cl atom = 3	Trigonal bipyramid	T or arrow shapped (→) 
d.	$:XeOF_4$	$H = \frac{1}{2}(8+4+0) = 6$ $H = sp^3d^2$ *lp* at Xe atom = 1 *bp* at Xe atom = 5	Octahedral	Square pyramid 
e.	$:SO_2$	$H = \frac{1}{2}(6+0) = 3$ $H = sp^2$ *lp* at S atom = 1 *bp* at S atom = 2	Trigonal planar	Bent with bond angle <120° (as *lp*–*bp* repulsion is more than *bp*–*bp* repulsion) 
f.	SO_3	$H = \frac{1}{2}(6+0) = 3$ $H = sp^2$ *lp* at S atom = 0 *bp* at S atom = 3	Trigonal planar	Trigonal planar 
g.	$:IF_4^{\oplus}$	$H = \frac{1}{2}(7+4-1) = 5$ $H = sp^3d$ *lp* at I atom = 1 *bp* at I atom = 4	Trigonal bipyramid	See saw 
h.	$NH_4^{\oplus}$	$H = \frac{1}{2}(5+4-1) = 4$ $H = sp^3$ *lp* at N atom = 0 *bp* at N atom = 4	Tetrahedral	Tetrahedral 

ILLUSTRATION 2.24

Which *p* and *d* orbitals of central atoms are involved in the hybridisation of the following compounds.

a. $[PtCl_4]^{2-}$ b. AsF_5 c. IF_3 d. XeO_2F_2

e. $XeOF_4$ f. XeF_6 g. IF_7

Sol. For explanation, refer to Section 2.21.11.

a. Coordination number of Pt^{2+} is 4. Hybridisation at Pt^{2+} is dsp^2 (square planar). The orbitals involved in hybridisation are:

$dx^2-y^2\, sp^2$ or $dx^2-y^2+s+px+py$

b. Hybridisation at As atom $= \frac{1}{2}(V + M)$

$= \frac{1}{2}(5 + 5) = 5 = sp^3d.$

(Trigonal bipyramid)

The orbitals involved in hybridisation are $sp^3\ d_z^{\ 2}$.

c. Hybridisation at I atom $= \frac{1}{2}(7 + 3) = 5 = sp^3d.$

Geometry is trigonal bipyramid (Tbp). Due to 2 *lp* on I atom, it has T shape. The orbitals involved in hybridisation are, $sp^3\ d_z^{\ 2}$.

d. Hybridisation at Xe atom $= \frac{1}{2}(8 + 0 + 2) = 5 = sp^3d.$

Geometry is Tbp but due to 1 *lp*, it has see-saw shape, the orbitals involved in hybridisation are $sp^3\ d_z^{\ 2}$.

e. Hybridisation at Xe atom $= \frac{1}{2}(8 + 0 + 4) = 6 = sp^3d^2.$

Geometry is octahedral (OH), but due to 1 *lp* it has square pyramid shape. The orbitals involved in hybridisation are $sp^3, d_{x^2-y^2}, d_{z^2}$ or $(s + p_x + p_y + p_z + d_{x^2-y^2} + d_{z^2})$

f. Hybridisation at Xe atom $= \frac{1}{2}(8 + 6) = 7 = sp^3d^3$. Geometry is pentagonal bipyramid (Pbp) but due to 1 *lp* it has distorted octahedral shape.

The orbitals involved in hybridisation are sp^3, *dxy, dyz dxz* or $(s + p_x + p_y + p_z + dxy + dyz + dxz.)$

g. Hybridisation at I atom $= \frac{1}{2}(7 + 7) = 7 = sp^3d^3.$

Geometry and shape is pentagonal bipyramid (pbp), since I atoms do not have any *lp*'s. The orbitals involved in hybridisation are sp^3 *dxy dyz dxz* or $(s + p_x + p_y + p_z + dxy + dyz + dxz.)$

Concept Application Exercise 2.1

1. Write a Lewis structure for CCl_2F_2, one of the compounds indicated in the depletion of stratospheric ozone.
2. Write Lewis structure for the following:
   a. Ethene (C_2H_4), the most important reactant in polymer manufacture.
   b. Nitrogen (N_2), the most abundant atmospheric gas.
   c. Methanol (CH_4O), an important industrial alcohol that is being used as a gasoline alternative in car engines.
3. The dipole moment of LiH is 1.964×10^{-29} Cm and interatomic distance between Li and H in this molecule is 1.6 Å. What is the per cent ionic character in LiH?
4. Predict whether each of the following molecule has a dipole moment:
   a. BF_3 **b.** IBr **c.** CH_2Cl_2
5. The dipole moment of KCl is 3.36×10^{-29} Cm. The interatomic distance between $K^{\oplus}$ and $Cl^{\ominus}$ in this unit of KCl is 2.3×10^{-10} m. Calculate the percentage ionic character of KCl.
6. Account for the following observations:
   a. Ammonium salts are more soluble in water than the corresponding sodium salts.
   b. $BeCl_2$ is linear but $SnCl_2$ is angular.
   c. F_2 gas is more reactive than Cl_2 gas.
   d. The bond lengths of both O – O bonds in ozone are equal.
7. State whether the following are ionic or covalent?
   a. CaH_2 **b.** MgO **c.** Na_2CO_3 **d.** NH_4Cl
   e. HCl **f.** $CaCl_2$ **g.** Na_2S **h.** $SnCl_4$
   i. Diamond **j.** CaC_2 **k.** NaH **l.** C_2H_2
8. Identify, which of them are polar and non-polar:
   a. HF **b.** $BeCl_2$ **c.** $HgCl_2$ **d.** NH_3
   e. H_2O **f.** N_2 **g.** $AlCl_3$ **h.** CCl_4
   i. Cl_2 **j.** $SiCl_4$.
9. Give reasons for the following:
   a. PF_5 is known but NF_3 is not.
   b. H_2O is a good solvent.
   c. BF_3 is non-polar but planar.
   d. NF_3 is pyramidal and polar.
   e. Carbon – oxygen (C – O) bond lengths are equal in Na_2CO_3.
   f. MgF_2 is more soluble in water than $MgCl_2$.
10. Give reasons for the following:
    a. CO_2 has no dipole moment but SO_2 and H_2O have considerable dipole moments.
    b. Carbon has two unpaired electrons in the outermost orbit, but it is tetravalent in organic compound.
    c. CaF_2 is more ionic than CaI_2.
    d. Sigma bonds are stronger than *pi* bonds.
    e. C_2H_4 is planar while C_2H_2 is linear.
    f. H_2O is more polar than H_2S.
    g. Ionic compounds do not conduct electricity in solid state, but they conduct electricity in solution or in molten state.
11. Indicate whether the following pairs of elements form ionic or covalent compounds. Also, write their molecular formula.
    a. C and S **b.** Na and Cl **c.** S and O **d.** Ca and H
12. Arrange the following as directed:
    a. N_2, O_2, F_2, Cl_2 (Decreasing order of bond energy)
    b. S – O, N – Cl, Mg – O, As – F (Decreasing polarity of bonds)
    c. *s, p,* sp^3, sp^2, *sp* (Decreasing order of energy of orbitals)
    d. HF, HCl, HBr, HI (Decreasing order of dipole moments)

13. Explain the following:
   a. The central C–C bond in Buta-1, 3-diene is shorter than that of *n*-butane.
   b. Why the dipole moment of *cis*-1, 2-dichloroethene is greater than that of *trans*-1, 2-dichloroethene.
   c. $ClF_2^{\ominus}$ is linear, but $ClF_2^{\oplus}$ is bent.
   d. Two different bond lengths are observed in PF_5 but only one bond length is observed in SF_6.
14. Arrange the following in decreasing order of dipole moment.
   a. 1. Toluene 2. *m*-Dichlorobenzene 3. *o*-Dichlorobenzene 4. *p*-Dichlorobenzene
   b. 1. BF_3 2. H_2S, 3. H_2O.
   c. 1. *cis*-1-Chloropropene
      2. *Trans*-1-Chloropropene
      3. 1, 1-Dichloroethene
15. Predict the shape of the following Xenon compounds.
   a. XeO_3 b. $XeOF_4$ c. XeO_2F_2
16. Considering *X*-axis as the internuclear axis, which out of the following will form a sigma bond?
   a. 1*s* and 1*s* b. 1*s* and $2p_x$
   c. $2p_y$ and $2p_y$ d. $2p_x$ and $2p_y$
   e. 1*s* and 2*s*

ANSWERS

3. 76.8% 5. ≈91%

2.23 INTERMOLECULAR FORCES

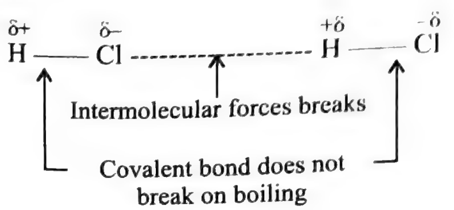
Intermolecular forces are the forces of attraction and repulsion existing among the molecules of a substance (gaseous, liquid or solid). This term does not include the electrostatic forces that exist between two oppositely charged ions and the forces that hold atoms of a molecule together, i.e. covalent bonds.

Intermolecular forces are responsible for the structural characteristics and physical properties of the substance, whereas intramolecular forces (i.e. forces which exist within the same molecule) affect the chemical properties of the substance.

$$[\text{Intermolecular forces}] \propto \begin{Bmatrix}\text{Melting and boiling} \\ \text{point of the substance}\end{Bmatrix}$$

At the boiling point, the heat absorbed is used to break the intermolecular forces to convert liquid into vapour.

When an ionic compound melts, the ionic bond breaks. However, when a molecular substance melts or boils, the intermolecular forces of attraction do not break the covalent bonds e.g. in case of HCl molecule.



2.23.1 TYPES OF INTERMOLECULAR FORCES AND THEIR CHARACTERISTICS

The intermolecular forces occur due to any one of the following interactions:

1. Ion–dipole
2. Ion-induced dipole (OR) Debye forces
   [These are non van der Waals forces.]
3. Dispersion forces (OR) London forces (OR) Instantaneous dipole-induced dipole (OR) Momentary dipole.
4. Dipole–dipole forces or Keesom forces
5. Dipole-induced dipole.
   [These are collectively called van der Waals forces.]
6. Hydrogen bonding [It is a strong type of dipole–dipole interaction. Only a few elements can participate in hydrogen bond. Therefore, it is treated as a seperate category.]

The different types of forces are briefly explained below:

1. **Non van der Waals forces:**
   a. **Ion–Dipole Interactions:** This is the attraction between an ion (cation or anion) and a polar molecule. For example, when NaCl is dissolved in water, the polar water molecules are attracted towards $Na^{\oplus}$ ion as well as towards $Cl^{\ominus}$ ion (a process called **hydration of ions**). The strength of this interaction depends upon the charge and size of the ion and the magnitude of dipole moment and size of the polar molecule. Due to greater charge density on the cation, this interaction is usually stronger with the cation than with the anion having the same charge but bigger size. Further, CCl_4, being non-polar cannot interact with $Na^{\oplus}$ and $Cl^{\ominus}$ ions. Hence, NaCl is insoluble in CCl_4.

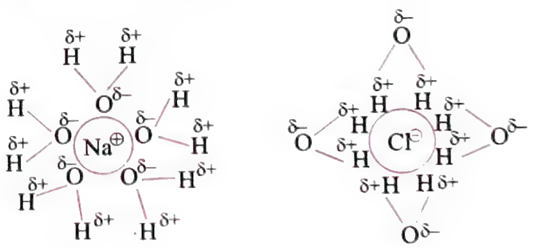


Fig. 2.53 Ion–dipole attractions between $Na^{\oplus}$ and H_2O molecules and $Cl^{\ominus}$ ion and H_2O molecule

   b. **Ion-induced dipole interactions:** A non-polar molecule may be polarised by the presence of an ion near it, i.e. it becomes an induced dipole. The interactions between them are called ion-induced dipole interactions. The strength of these interactions depends upon the charge on the ion and the ease with which the non-polar molecule gets polarised. A cation polarises the molecule by attraction of the electron cloud whereas an anion does it by repulsion. For example, in the presence of nitrate ion ($NO_3^{\ominus}$), iodine molecule (I_2), which is non-polar, gets polarised as $\left(\overset{\delta+}{I} - \overset{\delta-}{I}\right)$.

Fig. 2.54 Ion-induced dipole attractions between $NO_3^{\ominus}$ ion and I_2 molecule

2. van der Waals forces:

a. Dispersion or London forces: Dispersion forces are interparticle forces among the monatomic or non-polar molecules such as N_2, He, CO_2, etc. Atoms and non-polar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentarily even in such atoms and molecules. This can be understood from the following illustration. Suppose we have two atoms A and B in the close vicinity of each other [Fig. 2.55 (a)]. It may so happen that electronic charge distribution in one of the atoms, say A, becomes momentarily unsymmetrical, i.e. the charge cloud is more on one side than the other [Fig. 2.55 (b, c)]. This results in the development of instantaneous dipole on atom A for a very short time. This instantaneous or transient dipole distorts the electron density of the other atom B, which is close to it, and a consequence dipole is induced in atom B.

The temporary dipoles of atoms A and B attract each other. Similarly, *temporary dipoles are induced in molecules also*. This force of attraction was first proposed by the German physicist Fritz London, and for this reason the force of attraction between two temporary dipoles is known as *London force*.

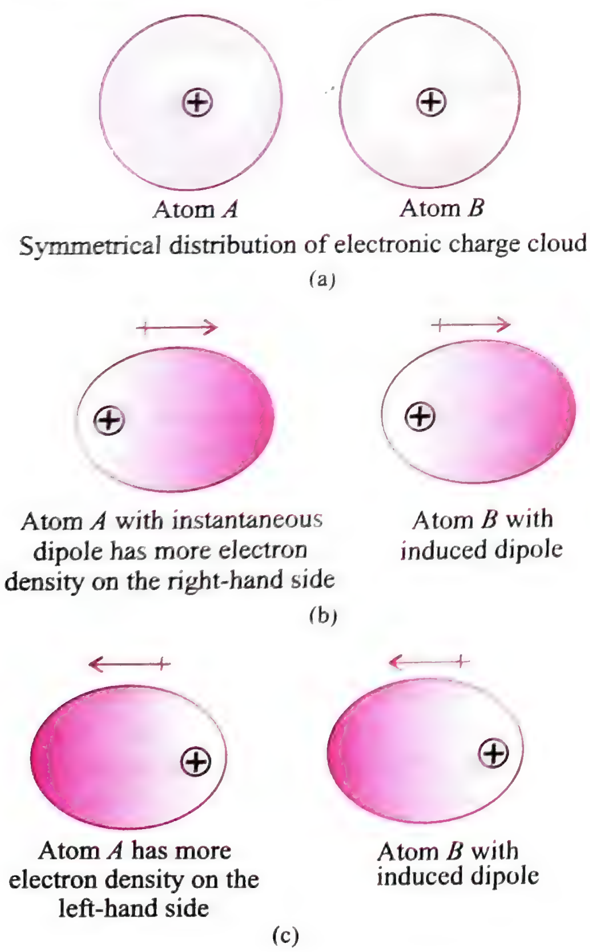


Fig. 2.55 Dispersion forces or London forces between two atoms

Another name of this force is *dispersion force*. These forces are always attractive.

In these forces, the interaction energy is inversely proportional to the sixth power of the distance between two interacting particles (i.e. $1/r^6$, where r is the distance between two particles). These forces are important only at short distances (~ 500 pm), and their magnitude depends on the polarisability of the particle.

The strength of these forces depends upon the following factors:

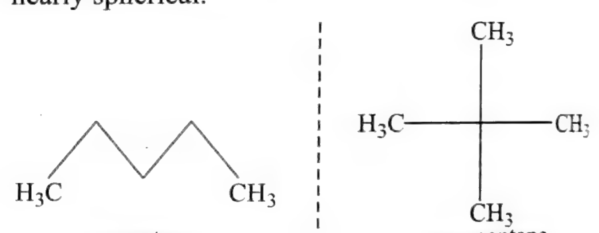
i. **Molecular size (molar mass):** Molecules having larger size or molar mass have higher magnitude of London forces.

ii. **Number of electrons:** Molecules with higher number of electrons have higher magnitude of London forces as compared to molecules with lesser number of electrons.

iii **Surface area of molecule:** With an increase in surface area, the strength of London forces also increases. For example, boiling point increases for CH_4 to GeH_4, i.e. CH_4 (112 K) < SiH_4 (161 K) < GeH_4 (183 K).

Therefore, if molecular mass and the number of electron increase, the intermolecular forces and boiling points also increase.

iv. For example, *n*-pentane and neopentane have the same molecular formula (C_5H_{12}), yet the boiling point of *n*-pentane is about 27°C higher than that of neo-pentane due to the difference in their surface area. The *n*-pentane is a zig-zag chain whereas neo-pentane is nearly spherical.



n-pentane (b.pt. = 36.2°C)

neo-pentane (b.pt. = 9.5°C)

The surface area of *n*-pentane is greater than that of neo-pentane. Hence, in the case of *n*-pentane, the overall attraction between molecules is greater because there are more sites of interaction. Thus, molecules are able to come in contact with the entire length of the molecule.

b. Dipole–dipole force: Dipole–dipole forces act among molecules possessing permanent dipole. Ends of dipoles possess 'partial charges' and these charges are shown by Greek letter delta (δ). Partial charges are always less than the unit electronic charge (1.6×10^{-19} C). Polar molecules interact with neighbouring molecules. Figure 2.56(a) shows electron cloud distribution in the dipole of hydrogen chloride, and Fig. 2.56(b) shows dipole–dipole interaction between two HCl molecules. This interaction is stronger than the London forces, but is weaker than the ion–ion interaction because only partial charges are involved. The attractive forces decrease with an increase in distance between the dipoles. As in the above case, the interaction energy is inversely proportional to the distance between two polar molecules.

Dipole–dipole interaction energy between two stationary polar molecules (as in solids) is proportional to $1/r^3$ and that between two rotating polar molecules is proportional to $1/r^6$, where r is the distance between the two molecules. Besides dipole–dipole interaction, polar molecules can also interact by London forces. The cumulative effect is that total intermolecular forces in polar molecules increases.

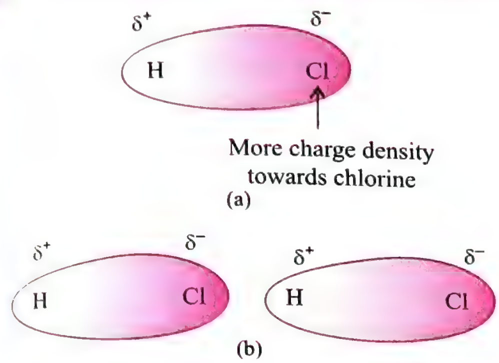


Fig. 2.56. (a) Distribution of electron cloud in HCl, a polar molecule. (b) Dipole–dipole interaction between two HCl molecules

The existence of these forces was studied by Keesom in 1912. Hence, these forces are called **Keesom forces.**

The magnitude of dipole–dipole forces in different polar molecules can be predicted on the basis of the polarity of the molecules, which in turn depends upon the electronegativities of the atoms present in the molecules and the geometry of the molecule (in case of polyatomic molecules, containing more than two atoms in a molecule). The polarities of the molecules are usually expressed in terms of dipole moments of the molecules. For example, dipole moments of PH_3 and H_2S are 0.55 D and 1.10 D, respectively, i.e. dipole moment of H_2S is double than that of PH_3. Thus, though both have nearly same molecular mass, the melting and boiling points of H_2S are higher than those of PH_3 (m.pt. PH_3 = 134°C, H_2S = –86°C, b.pt. PH_3 = – 88° C, H_2S = – 61°C).

SiH_4 also has nearly the same molecular but it is non- polar, i.e. its dipole moment is zero. Hence, its melting and boiling points are lower than both PH_3 and H_2S (m.pt. = – 185°C, b.pt. = – 111°C).

c. **Dipole-induced dipole forces:** This type of attractive forces operate between polar molecules having permanent dipole ($\mu > 0$) and molecules lacking permanent dipole ($\mu = 0$). Permanent dipole of a polar molecule induces a dipole on the electrically neutral molecule by deforming its electronic cloud (Fig. 2.57). Thus, an induced dipole is developed in the other molecule. In this case also, interaction energy is proportional to $1/r^6$, where r is the distance between two molecules. Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule.

As the size of molecule/atom increases, it can be easily polarised.

High polarisability increases the strength of attractive interactions.

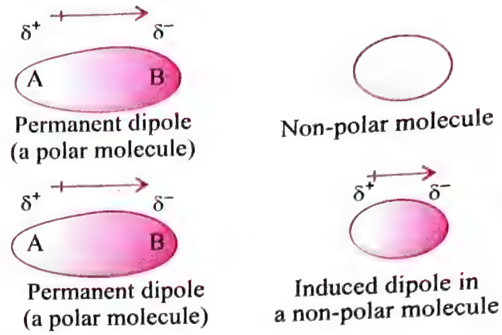


Fig. 2.57 Dipole-induced dipole interaction between permanent dipole and induced dipole

In this case also, the cumulative effect of dispersion forces and dipole–induced dipole interactions exists. The existence of these forces was studied by Debye (1920), and this effect was termed induction effect.

2.23.2 Strength of Chemical Forces

1. **Ionic bonding:** Ionic bonding is non-directional and is purely electrostatic. The attraction of one ion for another is completely independent of direction, but the sizes and numbers of ions determines the crystal structures. Ionic bonding is relatively insensitive to distance, the force between the ions is inversely proportional to square of the distance between them and hence decreases fairly rapidly with distance, but much less than most other chemical forces.
2. **Covalent bonding:** The covalent bond is strongly directional as a result of the overlap criterion for maximum bond strength.

   A typical covalent bond will have a strength of about 250–400 kJ mol^{-1}. The covalent bond energy qualitatively is a fairly short range force as the atoms are forced apart, the overlap decreases.

   Therefore, it is evident that covalent bond is stronger than all other chemical interaction with the exception of ionic bond.

2.23.3 Strength of Intermolecular Forces

Ion–dipole interaction has the strongest strength whereas the dispersion or London forces has the weakest strength among the intermolecular forces.

Thus, the decreasing order of their strength is: Ion–dipole > Dipole–dipole (Keesom forces) > Ion-induced dipole (Debye forces) > Dipole-induced dipole > Dispersion or London forces.

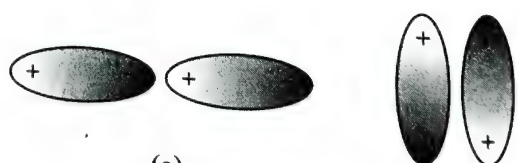
Three obvious sources of van der Waals forces are as follows:

1. Weak dipole–dipole electrostatic attractive forces which would exist in any molecule with permanent dipole, e.g. HCl, H_2O etc.
2. Weaker dipole-induced dipole interaction resulting from the polarisation of one molecule by the dipole of a neighbouring molecule.

3. For symmetrical molecules (e.g. Ne, Cl_2, H_2, CH_4 etc.) only London forces operate. Very weak dipoles even in non-polar molecules due to temporary fluctuations in the electron density distribution. These transient dipoles can now induce dipoles in neighbouring molecules producing a flux of weak temporary interactions.

Various forces acting on chemical species are summarised in Table 2.15.

Table 2.15 Summary of chemical forces and interactions

Type of interaction	Strength	Energy–distance function	Explanation
Ionic bond	Very very strong	$\frac{1}{r}$ (comparatively long range).	Neglecting repulsive forces, van der Waals forces, the energy of an ion pair is $E = \frac{\lvert Z^{\oplus} \rvert \lvert Z^{\ominus} \rvert e^2}{4\pi r \varepsilon_o}$, or $E \propto \frac{1}{r}$ strength of ionic bond is of the same order of magnitude as covalent bonds. The common notion that ionic bonds are considerably stronger than covalent bonds results from mistaken interpretations of melting and boiling phenomena.
Covalent bond	Very strong	Complex, but comparatively long range	Because of the complexity of the forces operating in the covalent bond, it is not possible to write a simple potential energy function as for the electrostatic forces such as ion–ion and dipole–dipole.
Intermolecular forces (non van der Waals interactions):			
Ion–dipole	Strong	$\frac{1}{r}$ (short range)	The potential energy of an ion–dipole interaction is given by $E = \frac{\lvert Z^{\pm} \rvert \mu e}{4\pi r^2 \varepsilon_o}$ or $E \propto \frac{1}{r^2}$ (where $Z^{\pm}$ is the charge on the ion and r is the distance between the ion and the molecular dipole, μ is the dipole moment). Ion–diple interactions are similar to ion–ion interaction, except that they are more sensitive, except that they are more sensitive to distance ($\frac{1}{r^2}$ instead of $\frac{1}{r}$) and tend to be somewhat weaker since the charges ($q^{\oplus}, q^{\ominus}$) comprising the dipole are usually considerably less than a full electronic charge.
Dipole–dipole	Moderately strong	$\frac{1}{r^3}$ (short range)	The energy of interaction of two dipoles is given by $E = \frac{-2\mu_1 \mu_2}{4\pi r^3 \varepsilon_o}$, or $E \propto \frac{1}{r^3}$ The energy corresponds to 'head to tail' (a) and antiparallel arrangement of dipoles (b).  (a) (b) The latter arrangement [i.e. (b)] is more stable if the molecules are not too 'fat'. Dipole–dipole interactions tend to be even weaker than ion–dipole interactions and to fall off more rapidly with distance $\left(\frac{1}{r^3}\right)$. Like ion–dipole forces, they are directional in the sense that there are certain preferred orientations and they are responsible for the association and structure of polar liquids.

Intermolecular forces (van der Waals interaction):			
Ion–induced dipole	Weak	$\frac{1}{r^4}$ (very short range)	The energy of such interaction is $E = -\frac{Z^2 \alpha e^2}{2 r^4}$, or $E \propto \frac{1}{r^4}$. The polarisation of the neutral species will depend upon its inherent polrisability ('softness') α, and on the polarising field afforded by the charged ion, $Z^{\pm}$. These interactions tend to be very weak since the polarisabilities of most species are not large. The energy varies inversely with powers of r, they are effective only at a very short distance.
Dipole–induced dipole	Very weak	$\frac{1}{r^6}$ (extremely short range)	Like ion-induced dipole, a dipole can induce another dipole in an otherwise uncharged, non-polar species. The energy of such interaction is $E = \frac{-\mu^2 \alpha}{r^6}$, or $E \propto \frac{1}{r^6}$ where μ is the moment of inducing dipole. Like ion-induced dipole, these interactions are very weak. The energy varies inversely with powers of r, they are effective only at a very short distance.
London dispersion force (or) Instantaneous dipole–induced dipole interactions	Very weak	$\frac{1}{r^6}$ (extremely short range)	The energy of such interaction is $E = -\frac{-2\bar{\mu}\alpha}{r^6}$, or $E \propto \frac{1}{r^6}$ where $\bar{\mu}$ is the mean instantaneous dipole. These interactions are extremely short range in action (depending upon $1/r^6$) and the weakest of all attractive forces. These forces increase rapidly with molecular weight (or molecular volume) and the number of polarisable electrons. Molecular weight is not important in determining the magnitude of London forces for isotopes of hydrogen as well as similar compounds, such as hydrocarbons containing different isotopes of hydrogen. For example: **i.** H_2 (MW = 2), b.pt. = 20 K **ii.** D_2 (MW = 4, a factor of two different), b.pt. = 23 K **iii.** T_2 (MW = 6), b.pt. = 25 K Fluoro carbons have low boiling points because tightly held electrons in the F atoms have a small polarisability since London forces increase with increasing size and there is no limit to the size of molecules, these forces can become rather large, in general, however, they are weak.

ILLUSTRATION 2.25

a. Which among the following has highest boiling point and why?

b. Explain why boiling point of n-alkanes increases regularly with the increase in the number of carbon atoms.

Sol.

a. Xe has highest van der Waals force because of having more electrons and large surface area.

b. This can be explained on the basis of inter particle forces. The principal intermolecular force in alkane is London dispersion forces. With the increase in number of carbon atoms, the molecular mass and molecular size increase. This results in increases in magnitude of London dispersion forces. Consequently, the boiling point also increases.

ILLUSTRATION 2.26

a. Which of the following intermolecular force is van der Waals interaction:

i. Ion–dipole **ii.** Dipole–Dipole
iii. Ion-induced dipole **iv.** All

b. Which of the following intermolecular forces is non-van der Waals interaction:

i. Dipole-induced dipole
ii. Instantaneous dipole-induced dipole
iii. Ion-induced dipole
iv. None

c. Which of the following intermolecular forces have a potential energy–distance function as $E \propto \frac{1}{r^2}$

i. Ion–dipole
ii. Dipole–dipole
iii. Ion-induced dipole
iv. London dispersion forces.

Sol. **a.** (iii) **b.** (iv) **c.** (i)

2.23.4 Thermal Energy

Thermal energy is the energy of a body arising from the motion of its atoms or molecules. It is directly proportional to the temperature of the substance. It is the measure of the average kinetic energy of the particles of matter and is thus responsible for the movement of particles. This movement of particles is called thermal motion.

2.23.5 Intermolecular Forces and Thermal Energy

We have already learnt that intermolecular forces tend to keep molecules together but thermal energy tends to keep them apart. Three states of matter are the result of balance between intermolecular forces and the thermal energy of the molecules.

In the gaseous state, molecular interactions are very weak. Gas molecules do not cling together as in liquids or solids unless the thermal energy of the gas is reduced by lowering its temperature. A decrease in thermal energy causes molecules to come close, and they gradually develop intermolecular attraction till the gas condenses first into liquid and finally into solid. Gases do not liquefy only on compression, although molecules come very close to each other and intermolecular forces operate to the maximum. However, by reducing the thermal energy of molecules by lowering the temperature, gases can be very easily liquefied.

In the liquid state, a fine balance exists between attractive forces and thermal energy. As a result, molecules can break away from one another and at the same time get attracted to other molecules. An increase in temperature results in an increase in thermal energy, and ultimately a stage reaches when the molecules fall apart and behave almost as independent entities. This stage is referred to as gaseous state. On the other hand, a decrease in temperature decreases thermal energy. On further compression, the intermolecular interaction increases. At this stage, the molecules of liquid cling closely and this stage is referred to as solid state.

In the solid state, molecular interactions are very strong, but the molecular motion is restricted to oscillatory or vibratory movement about their mean position. The molecules possess low thermal energy and, therefore, cannot break molecules free from mutual attraction. When we heat a solid, thermal energy gradually increases, which weakens the intermolecular forces and causes them to move apart. When the average distance between the molecules increases beyond 10^{-7} cm, the solid melts into liquid. Further rise in temperature results in further increase in thermal energy, which further weakens the intermolecular forces and causes them to move apart and results in gaseous state.

Predominance of thermal energy and the molecular interaction energy of a substance in three states is depicted as follows:

Gas $\longrightarrow$ Liquid $\longrightarrow$ Solid

Predominance of intermolecular interactions

Gas $\longleftarrow$ Liquid $\longleftarrow$ Solid

Predominance of thermal energy

Fig. 2.58 Predominance of intermolecular interactions and thermal energy

2.23.6 Hydrogen Bonding

1. **Hydrogen bond:** Whenever a molecule contains a hydrogen atom linked to a highly electronegative atom (such as F, O or N), this atom attracts the shared pair of electrons more and so this end of the molecule becomes slightly negative while the other end (i.e. H end) becomes slightly positive. The negative end of one molecule attracts the positive end of the other and as a result, a weak bond is formed between them. This bond is called hydrogen bond. It is represented by the dotted lines as shown below:

$$\overset{\delta+}{H}-\overset{\delta-}{X}\cdots\cdots\cdots\overset{\delta+}{H}-\overset{\delta-}{X}\cdots\cdots\cdots\overset{\delta+}{H}-\overset{\delta-}{X}$$

Thus, as a result of hydrogen bonding, an H atom links the two electronegative atoms simultaneously, one by a covalent bond and the other by a hydrogen bond. Hence, it is said to form a hydrogen bridge.

2. **Conditions for hydrogen bonding:** In the formation of a hydrogen bond, the following conditions must be fulfilled:
   a. The molecule must contain a highly electronegative atom linked to H atom. The higher the electronegativity, more is the polarisation of the molecule.
   b. The size of the electronegative atom should be small. The smaller the size, the greater is the electrostatic attraction.

Thus, only F, O and N atoms can form hydrogen bonds, as these atoms are small in size and have high electronegativities.

Chlorine, having the same electronegativity as that of nitrogen, does not form hydrogen bond due to its large size. But in organic compounds Cl forms H-bonding due to the difference in EN's between C and Cl.

2.23.7 Types of H-Bonding

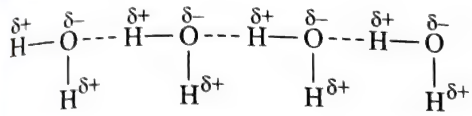
There are two types of H-bonding:

1. **Intermolecular hydrogen bonding:** When hydrogen bonding takes place between different molecules of the same or different compounds, it is called intermolecular hydrogen bonding, e.g. HF, H_2O, ROH (same compound), and water-alcohol, ammonia and water (different compounds), etc.
2. **Intramolecular hydrogen bonding:** The hydrogen bonding which takes place within a molecule itself is called intramolecular hydrogen bonding (or chelation). It takes place in compounds containing two groups such that one group contains a H atom linked to an electronegative atom and the other group contains a highly electronegative

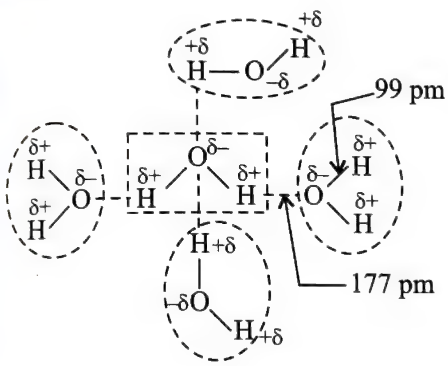
atom linked to a lesser electronegative atom. The bond is formed between the H atom of one group with the more electronegative atom of the other group.

2.23.8 Some Examples of Intermolecular H-Bonding

1. **In water molecules:** Due to polar nature of H_2O, there is association of water molecules giving a liquid state of abnormally high b.pt.

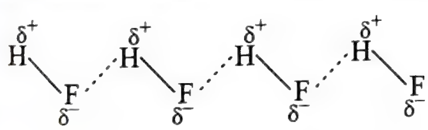


It was observed that one water molecule is joined to four water molecules, two with H-atoms and other two with O-atoms. Thus, coordination number of water molecules in water is four.

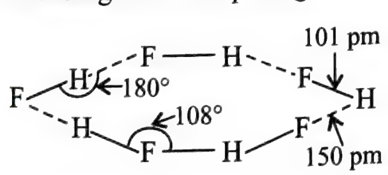


When ice is formed from liquid water, some air gap is formed (in tetrahedral packing of water molecules). Due to this volume of ice is greater than liquid water and thus ice is lighter than water. Thus, the density decreases when ice is formed. Reversely when ice melts, density increases but only up to 4°C.

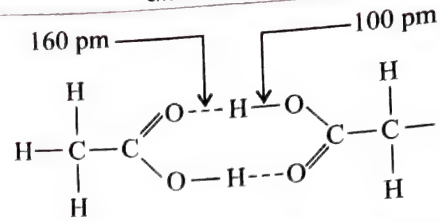
2. **In hydrofluoric acid (HF):** There is again association by H-bonding. Each HF molecule forms two H-bonding with two other HF molecules. This is due to the fact that size of F atom is so small that it cannot accommodate four HF molecules around it unlike H_2O which forms 4 H-bonds.



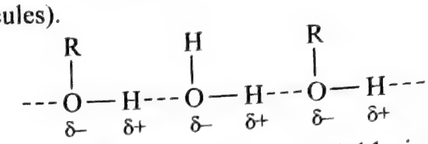
However in the *gaseous state*, several polymeric forms of the HF molecules exist in which the monomers are held together through H-bonding to form a pentagonal arrangement.



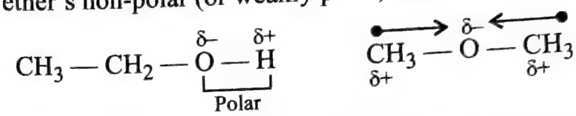
3. There is also similar H-bonding in alcohol (R — OH), ammonia (NH_3) and phenol (C_6H_5OH) molecules.
4. Carboxylic acid dimerises in gaseous state or in solvents of low dielectric constant, e.g. in benzene due to H-bonding.



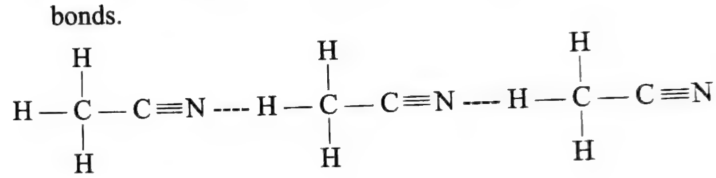
5. Alchol is said to be highly soluble in water due to crossed intermolecular H-bonding (between H_2O and R–OH molecules).

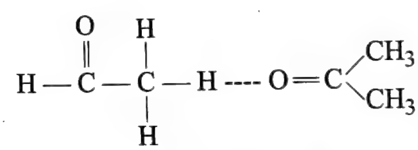


However, isomeric ether is less soluble in water due to ether's non-polar (or weakly polar) nature.



6. Though the hydrogen atoms in a methyl groups are not polarised, if an electronegative group like chloro, carbonyl nitro or cyano is attached to it, the C–H bond gets polarised due to the inductive effect and the hydrogen atom becomes slightly acidic resulting in the formation of weak hydrogen bonds.





7. **Cyanides and isocyanides:** Cyanides have a pleasant odour but alkyl isocyanides have a very unpleasant odour.
   a. **Boiling points:** Both the (– CN) and (– NC) groups are highly polar. As a result, they have strong intermolecular dipole–dipole interactions, and hence have higher boiling masses.

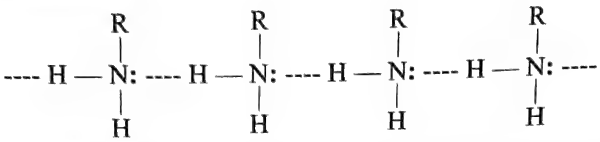
      Alkyl isocyanides have usually boiling points than their corresponding alkyl cyanides. This is because alkyl isocyanides have a lower dipole moment (approximately 3 D) as compared to those of alkyl cyanides (approximately 4 D).
   b. **Solubility:** The lower alkyl cyanides are soluble in H_2O due to H-bonds.

      $R—C\equiv N$ .... $H—O—H$ .... $N\equiv C—R$

      However, as the size of alkyl groups increases, the solubility decreases due to an increase in the hydrocarbon portion of the molecule. For example, acetonitrile ($CH_3 — C\equiv N$) is miscible with H_2O, propiononitrile ($C_2H_5C\equiv N$) is fairly soluble, but higher members are practically insoluble. However all cyanides are highly soluble in organic solvents.

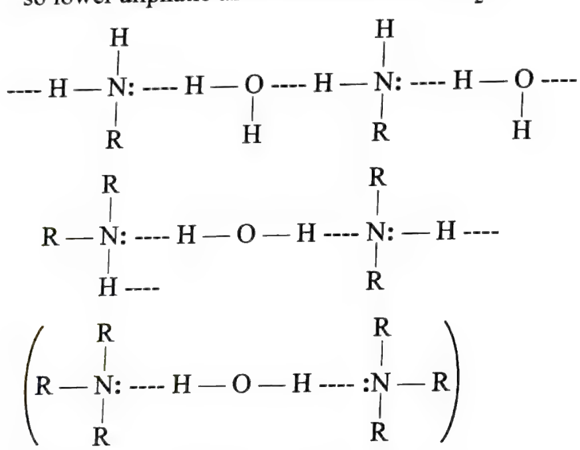
Alkyl isocyanides, on the other hand, are insoluble in H_2O. This is because the nitrogen atom does not have a lone pair of electrons and hence cannot form H-bonds.

8. **Amines:** Amines have higher boiling points than hydrocarbons of camparable molecular masses. This is due to the reason that amines, being polar, form intermolecular H-bonds (except 3° amines) and thus exist as associated molecule.



a. **Boiling points:** Furthermore, EN of N is lower than oxygen. Therefore, amines form weaker H-bonds as compared to acids and alcohols. As a result, amines are not associated to the extent of alcohols and acids, and hence the boiling points of amines are lower than those of alcohols and acids of comparable molecular masses.

b. **Solubility:** 1°, 2° and 3° amines form H-bonds with H_2O, so lower aliphatic amines are soluble in H_2O.



Methyl amines and ethyl amines are gases, but they are highly soluble in H_2O. That is why they are sold in the market as their 34% aqueous solution. However, as the size of the alkyl group increases, the solubility decreases due to the corresponding increase in the hydrocarbond part of the molecule. Aromatic amines are insoluble in H_2O due to the larger hydrocarbon part which tends to retard the formation of H-bonds.

2.23.9 Strength of Hydrogen Bond

H-bond is a very weak bond and its strength is intermediate between the weak van der Waals forces and strong covalent bonds.

Note: Electrostatic force > covalent bond > H-bond > van der Waals forces

i. Electrostatic force of attraction is that which holds the ions together in an ionic crystal.

ii. Covalent bond (force) is that which holds the atoms together in a covalent crystal.

iii. van der Waals forces is that which holds the molecules together in a molecular crystal.

The dissociation energy of the H-bond depends upon:

1. The attraction of the shared pair of electrons.
2. The EN of the atom.
3. The bond dissociation of H.....F, H.....O and H.....N are 41.8, 29.3 and 12.6 kJ mol^{-1} respectively.
4. Thus, the bond dissociation energy of a covalent bond is 209–418 kJ mol^{-1}, whereas that for H-bonds is only 12.6–41.8 kJ mol^{-1}.

2.23.10 Difference Between H-Bond and Covalent Bond

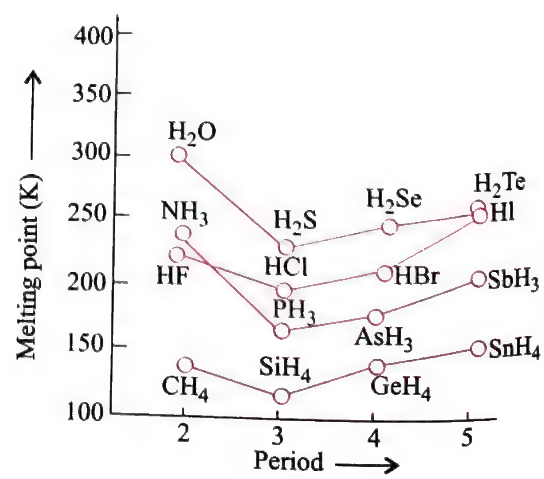
The main points of differences are given below:

	Hydrogen bond		Covalent bond
1.	It involves dipole–dipole attractive interactions.	1.	It involves sharing of electrons.
2.	It is formed between a H-atom and a highly EN atom such as F, O and N, which have small size also.	2.	It is formed between two EN atoms which may be of the same element or of different elements.
3.	The strength of H-bond is very small and lies between 12.6–41.8 kJ mol^{-1}.	3.	The strength of covalent bond is sufficiently high and lies between 209 and 418 kJ mol^{-1}.

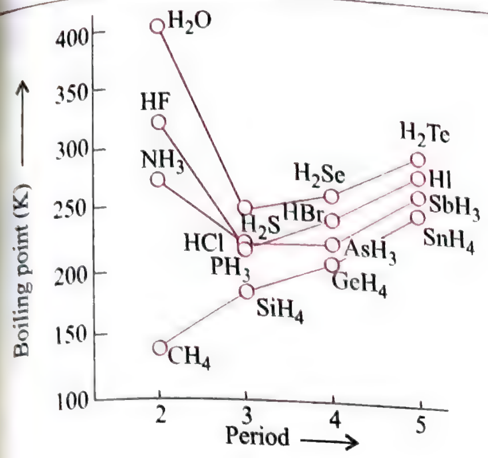
2.23.11 Consequences of Intermolecular H-Bonding

Some of the properties affected by H-bonds are as follows:

1. **High melting and boiling points:** The compounds having H-bonding show abnormally high melting and boiling points, as shown in Figs. 2.59(a) and (b) for the elements of groups 14, 15, 16 and 17.



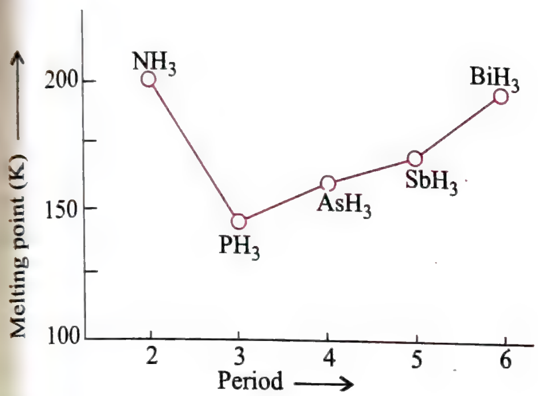
(a)



(b)

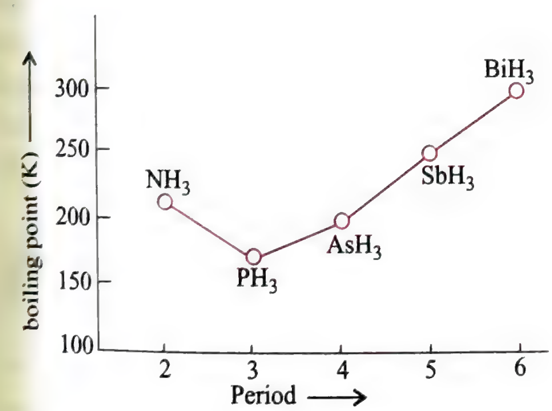
Fig. 2.59 (a and b) Melting and boiling points of elements of groups 14, 15, 16 and 17

2. **Explanation of melting and boiling points of hydrides of group 15** [Figs. 2.60(a) and (b)].



(a)

[**Melting point:** NH_3 (195.2) > BiH_3 (≈ 190) > SbH_3 (185) > AsH_3 (156.7) > PH_3 (139.5) K]



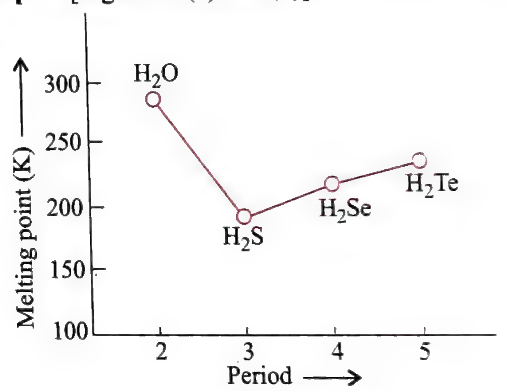
(b)

[**Boiling point:** BiH_3 (290) > SbH_3 (254.6) > NH_3 (238.5) > AsH_3 (210.6) > PH_3 (185.5) K]

Fig. 2.60 (a) and (b) Melting and boiling points of hydrides of group 15

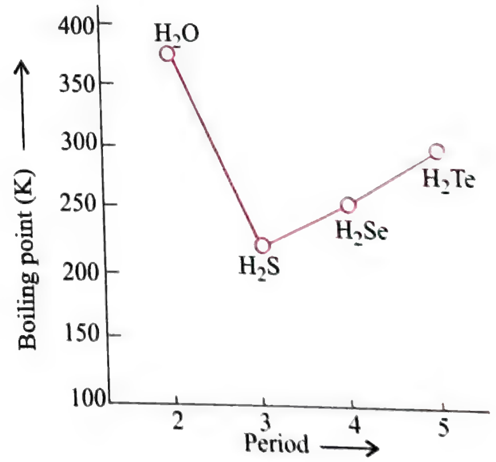
Explanation of hydrides of group 15	
Melting point	**Boiling point**
The m.pt. of NH_3 is the highest in the hydrides of group 15, due to intermolecular H-bonding. In this case increased molecular masses of BiH_3 and SbH_3 do not affect so much the m.pt. of NH_3. Because the increased van der Waals forces are not so strong in the solid state as they are in liquid state. (OR) The H-bonding in NH_3 is stronger in the solid state than in the liquid or gaseous state.	The boiling point of NH_3 is slightly lower than those of BiH_3 and SbH_3, due to their high molecular mass as compared to that of NH_3. The increased molecular masses of BiH_3 and SbH_3 increases the van der Waals forces of attraction in liquid state. (OR) The H-bonding in NH_3 is weaker in the liquid or gaseous state than in solid state.

3. **Explanation of melting and boiling points of hydrides of group 16** [Figs. 2.61(a) and (b)]



(a)

[**Melting point:** H_2O (273) > H_2Te (222) > H_2Se (208) > H_2S (188) K]



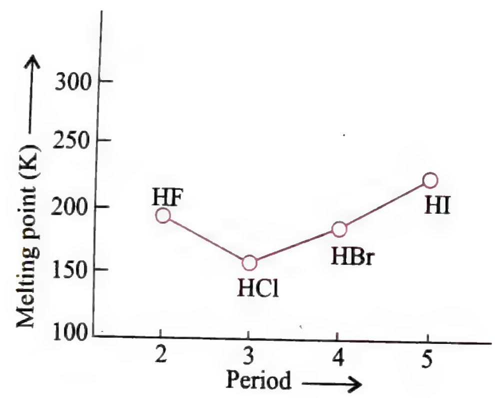
(b)

[**Boiling point:** H_2O (373) > H_2Te (269) > H_2Se (232) > H_2S (213) K]

Fig. 2.61 (a) and (b) Melting and boiling points of hydrides of group 16

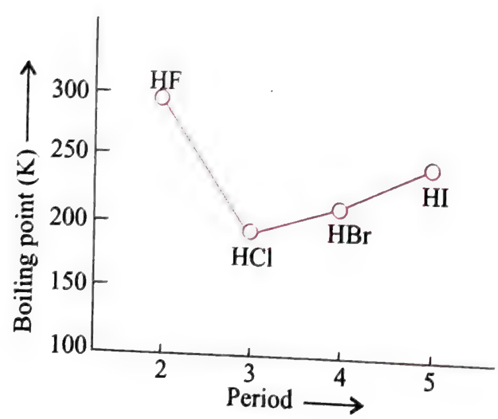
Explanation of m.pt. and b.pt. of hydrides of group 16	
Melting point	**Boiling point**
The melting point of H_2O is the highest in the hydrides of group 16 due to intermolecular H-bonding. The H-bonding in H_2O is greater than that of HF and NH_3. Since the EN of F > O > N. But greater H-bonding in H_2O than HF is due to the reason that H_2O forms four H-bonds while H–F forms two H-bonds. Hence, the increased molecular masses of H_2Te does not effect the m.pt. of H_2O.	Same explanation as in the melting point.

4. Explanation of melting and boiling points of hydrides of group 17 [Figs. 2.62(a) and (b)].



(a)

[**Melting point:** HI (222) > HF (190) > HBr (185) > HCl (159) K]



(b)

[HF (293) > HI (283) > HBr (206) > HCl (189) K]

Fig. 2.62 (a) and (b) Melting and boiling points of hydrides of group 17

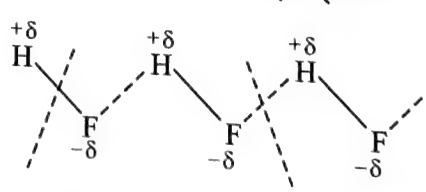
Explanation of m.pt. and b.pt. of hydrides of group 17	
Melting point	**Boiling point**
The melting point of HF is slightly lower than that of HI, due to increased molecular mass of HI which increases the van der Waals forces of attraction. (OR) H-bonding in HF is weaker in the solid state than in liquid or gaseous state.	The boiling point of HF is the highest as usual due to the strong H-bonding of HF in the liquid or gaseous state than in the solid state.

5. Comparison of the melting point and boiling point of NH_3, H_2O and HF:

Melting point	Boiling point
H_2O (273) > NH_3 (195.2) > HF (190) K	H_2O (373) > HF (293) > NH_3 (238.5) K
EN of F > O > N. So, HF should have stronger H-bonding. But both H_2O and NH_3 form four H-bonding while HF forms only two H-bonding. Moreover, the H-bonding in NH_3 is stronger in the solid state than in the liquid or gaseous state. Whereas the H-bond in HF is weaker in the solid state than in the liquid or gaseous state. Hence the m.pt. of H_2O > NH_3 > HF as given above.	Both H_2O and NH_3 form four H-bonding while HF forms only two H-bonding. But H-bonding of HF in the liquid or gaseous state is stronger than in solid state. Therefore, the boiling point of HF > b.pt. of NH_3. Hence, the boiling point of H_2O > HF > NH_3 as given above.

6. Existence of KHF_2 and non-existence of $KHCl_2$, $KHBr_2$ or KHI_2 (dissociation): In aqueous solution HF dissociates and gives the hydrogen difluoride in ($HF_2^{\ominus}$) instead of fluoride ion ($F^{\ominus}$). This is due to H-bonding in HF. This explains the existence of KHF_2.

$$H-F + H_2O \not\rightleftharpoons H_3O^{\oplus} + F^{\ominus} \text{ (does not occur)}$$



$$+ H_2O \longrightarrow HF_2^{\ominus} + H_3O^{\oplus}$$
(it occurs)

Whereas due to not so high EN and large size of Cl, Br and I, the molecules of HCl, HBr and HI do not form H-bonding. This explains the non-existence of compounds such as $KHCl_2$, $KHBr_2$ and KHI_2.

7. Formation of dimer (association): Carboxylic acids exist as dimer in gaseous state or in solvents of low dielectric

constant, e.g. in benzene, because of intermolecular H-bonding.

$$2(CH_3COOH) \rightleftharpoons \underset{\text{Dimer}}{(CH_3COOH)_2}$$

In this case, the number of particles is reduced due to dimerisation.

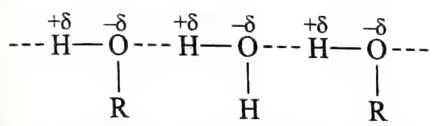
It can be undoubtedly stated here that if all the molecules of carboxylic acid (e.g. ethanoic acid), associate in benzene, then the colligative propertives (e.g. ΔT_b or ΔT_f) for ethanoic acid will be half of the normal value. The molar mass calculated on the basic of this ΔT_b or ΔT_f will, therefore, be twice the expected value. Such a molar mass that is either lower or higher than the expected or normal value is called as *abnormal mass*.

For example, the calculated molar mass (MW) of ethanoic acid is 60, whereas measured experimentally by colligative properties (e.g. ΔT_b or ΔT_f) was found to be 120.

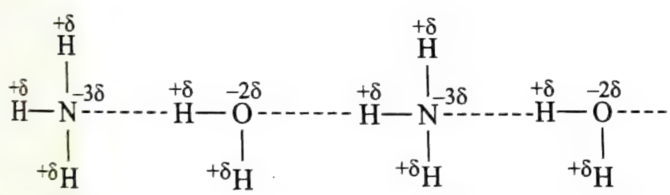
8. **Solubility in water:** The compounds which can form H-bonds with H_2O are soluble.

For example,

a. Lower alcohols are soluble in H_2O because of intermolecular H-bonding



b. NH_3 is soluble in H_2O because of intermolecular H-bonding.



9. **High viscosity and high surface tension:**
   a. The compounds which form intermolecular H-bonding exist as associated molecules.

   So, their flow becomes comparatively difficult resulting in high viscosity and high surface tension.

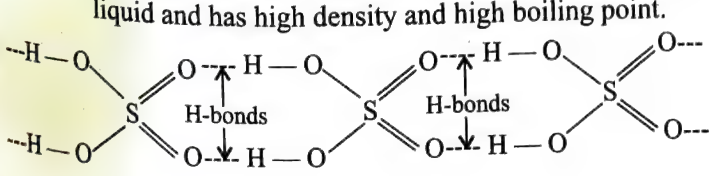
   b. Due to H-bonding, viscosity (η) of the liquid increases as given below in centipoises (CP).

   CH_3CH_2OH, $\eta = 2\,CP$

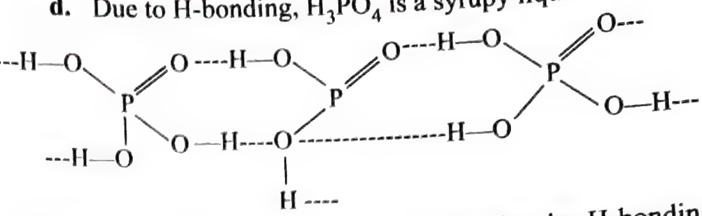
   CH_2OH–CH_2OH, $\eta = 17\,CP$

   CH_2OH–$CHOH$–CH_2OH, $\eta = 1070\,CP$

   c. Due to H-bonding, H_2SO_4 is colourless, viscous oily liquid and has high density and high boiling point.



   d. Due to H-bonding, H_3PO_4 is a syrupy liquid.



10. **Volatility:** Compounds having intermolecular H-bonding have higher boiling points, so they are less volatile. The enthalpies of vapourisation follow almost the same trend as shown by boiling points (Fig. 2.63).

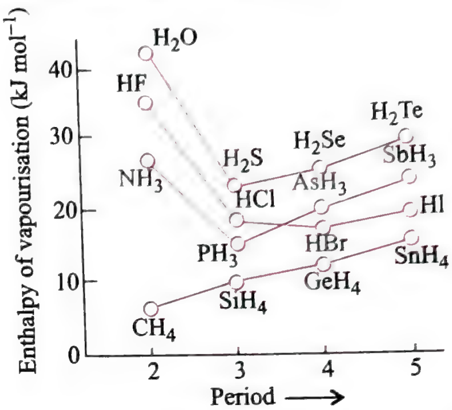


Fig. 2.63 Variation of enthalpies of vapourisation $\Delta H_{vap}H^{\ominus}$ of the hydrides of elements of periods 2 to 5

11. **H_2O is a liquid whereas H_2S, H_2Se and H_2Te are all gases at ordinary temperature:** Due to H-bonding in H_2O, it causes association of H_2O molecules with the result that the b.pt. of H_2O is more than that of the other compound. But in H_2S, H_2Se and H_2Te there is no such H-bonding.
12. **NH_3 has higher boiling point than PH_3:** Due to H-bonding in NH_3 but not in PH_3.
13. **C_2H_5OH (ethanol) has higher boiling point than diethyl ether ($H_5C_2-O-C_2H_5$):** Due to H-bonding in C_2H_5OH but not in $(C_2H_5-O-C_2H_5)$.
14. **Why ice floats on water:** Ice has lower density than H_2O, as explained below. Due to H-bonding in solid ice, it forms a cage-like structure of H_2O molecules (Fig. 2.64) in which each H_2O molecule is linked tetrahedrally to four H_2O molecules (Fig. 2.65). The molecules of H_2O are not so closely packed in the solid ice. When ice melts in cage-like structure, H-bonds break and molecules come closer to each other. Therefore, for the same mass of water, the volume decreases and hence density increases. Thus ice floats on water.

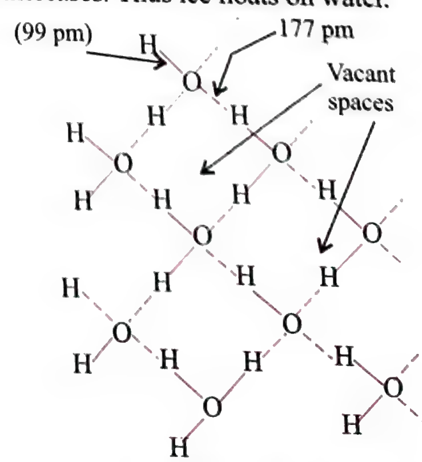


Fig. 2.64 Cage-like structure of H_2O in the ice

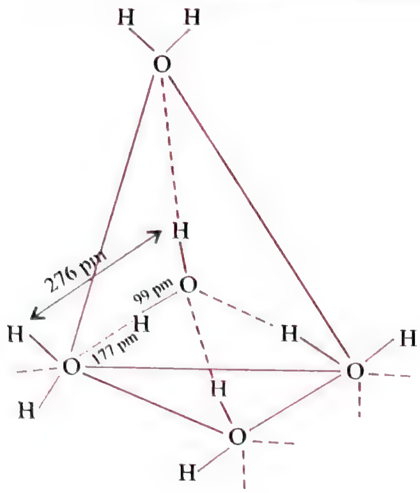


Fig. 2.65 Each H_2O molecule linked to four H_2O molecules tetrahedrally

a. In Fig 2.64, each O-atom is linked to four H atoms, two by covalent bonds and two by H-bonds.

b. In Fig 2.65, each H_2O is linked to four H_2O molecules tetrahedrally by H-bonds.

15. **Maximum density of H_2O at 4°C (or 277 K):** On heating, H-bonds start breaking and molecules come closer to each other, resulting in the decrease of volume and increase of density. This continues up to 277 K. At 277 K, all the H-bonds break and after 277 K, the increase in temperature increases the kinetic energy of H_2O molecules and thus H_2O molecules start moving apart from each other. This process increases the volume which means decreases in density. Hence, density of water is maximum at 277 K (Fig. 2.66).

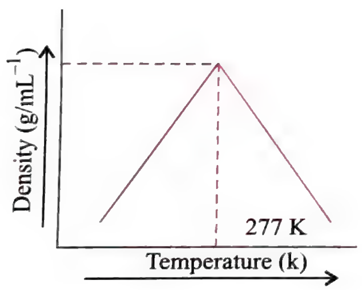
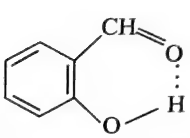


Fig. 2.66 Variation of density of H_2O with increase in temperature

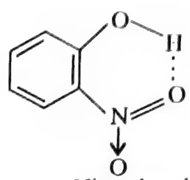
2.23.12 Some Examples of Intramolecular H-Bonding

This type of H-bonding occurs when polar H and electronegative atom are present in the same molecule.

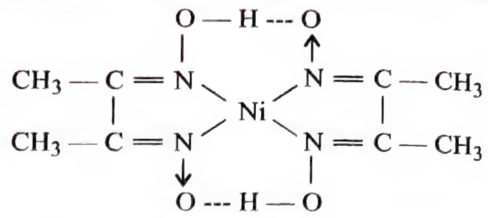
Examples:

1. 

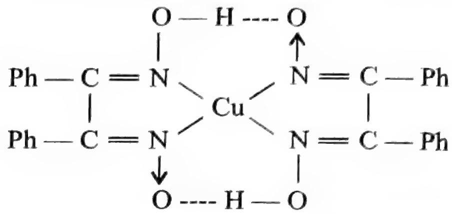
o-Hydroxy benzaldehyde

2. 

o-Nitro phenol

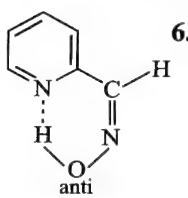
3. 

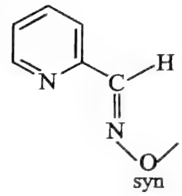
Nickel dimethyl glyoximate (a chelate)
(Red colour ppt., used as test for Ni^{2+} ion)

4. 

Benzoin oximate (a chelate) (Red colour ppt., used as a test for Cu^{2+} ion)

In case of anti-form of pyridine-2-carboxaldoxime (5) there is intramolecular hydrogen bonding, but it is not shown ... syn-form (6).

5. 

6. 

In this type of H-bonding, the bonding occurs within two atoms of same molecule. Such type of bonding generally occurs in aromatic organic compounds. It is also known as chelation.

2.23.13 Conditions for Intramolecular H-Bonding

The following conditions must be satisfied by intramolecular H-bonding:

1. The molecule should contain two groups such that one group contains H-atom linked to a highly EN-atom and other group should also contain a highly EN-atom linked to a lesser EN-atom.
2. The ring formed as a result of H-bonding should be planar.
3. A five- or six-membered ring should be formed.
4. Interacting atoms should be placed in such a way that there is minimum strain during the ring closure.
5. In case of *o*-, *m*- and *p*-isomers, H-bonding is formed at ortho (*o*-), position.

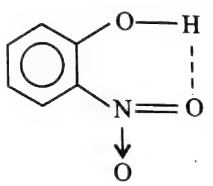
2.23.14 Effects of Intramolecular H-Bonding

1. Intramolecular H-bonding decreases melting and boiling points as well as their solubility in H_2O.
   For example, *o*-Chlorophenol, *o*-Nitrophenol and other *o*-derivatives (isomers of hydroxy, carbonyl and acids) show low boiling point as well as melting point as compared to their *m*- or *p*-derivatives (which shows intermolecular H-bonding).

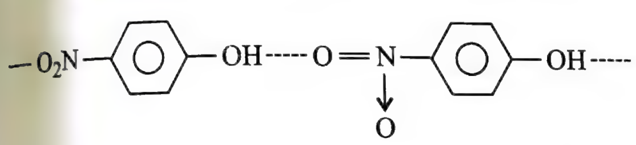
2. The solubility of all such compounds also decreases for the same reason, i.e. bonding between atoms of same molecules or chelation does not allow these molecules to form intermolecular H-bonds.

For example, in *o*-nitrophenol, (O–H) group makes intramolecular H-bonds with O-atom of NO_2 group and becomes unavailable for intermolecular H-bonding and hence it is very less soluble in H_2O.

In *o*-nitrophenol, intramolecular H-bonding occurs, which lowers the boiling point, whereas in *p*-nitro phenol, intermolecular H-bonding occurs, which increases the boiling point.

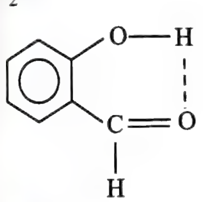


(Intramolecular H-bonding in *o*-nitro phenol)

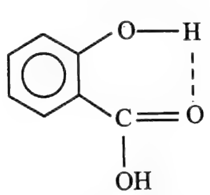


(Intermolecular H-bonding in *p*-nitro phenol)

Similarly, salicylaldehyde and salicyclic acid are soluble in hot water but their *m*- and *p*-isomers are soluble even in cold H_2O.



(Salicylaldehyde)



(Salicyclic acid)

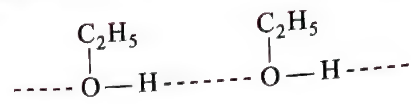
2.23.15 Significance of H-Bonding in Biological Systems

Water present in plants and animals (which is more than 50% by weight) is attached to proteins by hydrogen bonding. Similarly, the structures of proteins and nucleic acids are stabilised by hydrogen bonding.

ILLUSTRATION 2.27

Ethyl alcohol (C_2H_5OH) has higher boiling point than dimethyl ether ($CH_3 - O - CH_3$) although the molecular weight of both are same.

Sol. Though ethyle alcohol and dimethyl ether have the same molecular weight but in ethyl alcohol the hydrogen of the O-H groups forms intermolecular hydrogen bonding with the OH group in another molecule. But in case of ether the hydrogen is linked to C is not so electronegative to encourage the hydrogen to form hydrogen bonding.

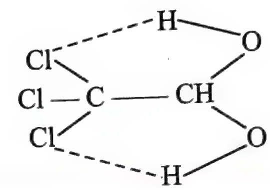


Due to intermolecular H-bonding, ethyl alcohol remains in the associated form and therefore boils at a higher temperature compared to dimethyl ether.

ILLUSTRATION 2.28

Explain unusual stability of chlorohydrate though a compound with two or more –OH groups present on one carbon atom is usually unstable.

Sol. The unusual stability of chloral hydrate has been attributed to – I effect of chlorine and to the formation of intramolecular hydrogen bonds ($Cl_3C–CH\ (OH)_2$).



Note: Here Cl-atom forms H-bond although EN of Cl is less than F. In organic molecule, H-bond with Cl-atom is considered due to the differences in the EN of Cl and C-atom.

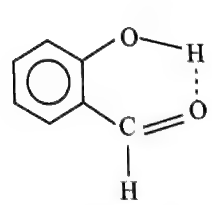
ILLUSTRATION 2.29

a. *o*-Hydroxy benzaldehyde is less soluble in water than *p*-hydroxy benzaldehyde.

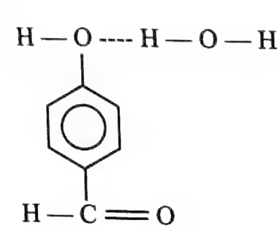
b. *o*-Hydroxy benzaldehyde is liquid at room temperature while *p*-hydroxy benzaldehyde is high melting solid.

Sol.

a. A substance is said to be soluble in water if it is capable of forming H-bonding with water molecule. In *o*-hydroxy benzaldehyde due to intramolecular chelation the –OH group is not available to form hydrogen bond with water hence it is sparingly soluble in water. On the other hand, the –OH group is available in *p*-hydroxy benzaldehyde to form H-bond with water and hence it is more soluble as compared to the *o*-isomer.

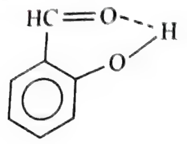


o-isomer



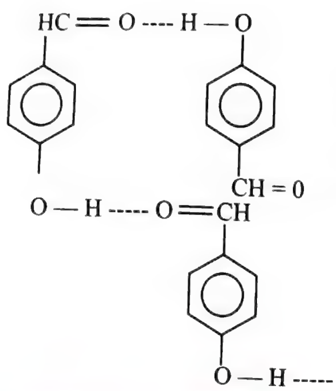
p-isomer

b. These are intramolecular H-bonding in *o*-hydroxy benzaldehyde while intermolecular H-bonding in *p*-hydroxybenzaldehyde.



(*o*-hydroxy benzaldehyde)

(H-bonding is within the same molecule, thus less interaction in comparison to *p*-hydroxy benzaldehyde, thus is liquid.)



(*p*-hydroxy benzaldehyde)

(In this case interaction increases close packing, thus becomes solid, so obviously high melting point.)

ILLUSTRATION 2.30

Explain the following:

a. Nitrogen and chlorine have almost same EN's but N forms H-bonding.

b. H_2O is liquid whereas H_2S is gas.

c. Compare the acidic strength of *o*-, *m*- and *p*- hydroxy benzoic acid.

d. NH_3 exists as liquid whereas HCl as gas.

e. Among the compounds CH_3COOH, NH_3, HF and CH_4 in which the strongest H-bonding is present.

f. Among HF, CH_3OH, N_2O_4 and CH_4 which would have intermolecular H-bonding.

g. Salt-like KHF_2 is stable but $KHCl_2$ is not known.

h. H_3PO_4 is a syrupy liquid.

i. H_2SO_4 is colourless, viscous oily liquid and has high boiling point.

j. Water forms four H-bonds as compared to two in HF. Explain?

k. Density of ice is less than that of water or ice floats over water.

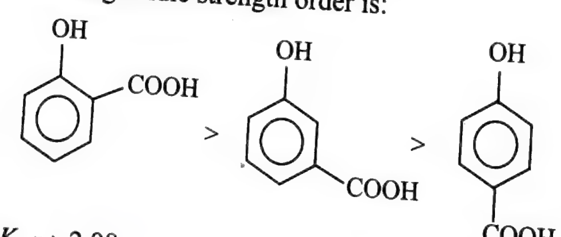
Sol.

a. Due to the large size of Cl, interacting with neighbouring molecules is not so strong.

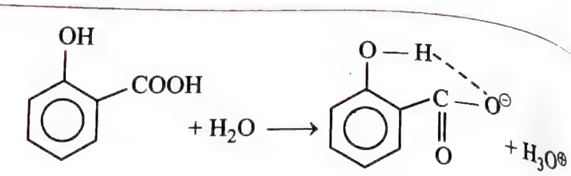
b. In H_2O, there are strong intermolecular forces due to extensive H-bonds. No such bonding exists in H_2S since EN of O > EN of S.

c. Strength of certain acids and bases can be explained on the basis of H-bonding. The abnormally high Ka or low pK_a value of *o*-hydroxybenzoic acid is due to the fact that the conjugate base is stabilised by H-bonding.

Decreasing acidic strength order is:



[$pK_a \Rightarrow$ 2.98   4.08   4.58]



d. The size of N atom is less than the size of Cl atom therefore electron density in N is more than that of Cl. So N forms H-bonding leading to association of molecule. Hence, NH_3 is liquid. H-bonding is not possible with Cl.

e. HF due to maximum EN of F. Decreasing order of strength of H–bonding.

$HF > NH_3 > CH_3COOH$ (exist as dimer) $> CH_4$.

f. HF and CH_3OH.

g. Refer to Section 2.23.11 (Point 6)

h. Refer to Section 2.23.11 [Point 9(d)]

i. Refer to Section 2.23.11 [Point 9(c)]

j. Refer to Section 2.23.8 (Point 1)

k. Refer to Section 2.23.11 (Point 14)

ILLUSTRATION 2.31

I. Arrange the compounds (a) in the order of decreasing boiling points and (b) in the order of decreasing solubility in water.

(A) (1) Ethanol, (2) Propane, (3) Pentanol

(B) (1) Butane, (2) 1,2,3-Pentanetriol (3) Butyl alcohol

(C) (1) Pentane, (2) Pentanol, (3) Hexanol

II. Arrange the following in the decreasing order of their boiling points.

(A) (1) C_3H_8, (2) C_2H_5OH, (3) $(CH_3)_2O$, (4) $HOH_2C—CH_2OH$

(B) (1) 3-Pentanol, (2) *n*-Pentane, (3) 2,2-Dimethyl propanol, (4) *n*-Pentanol

III. Arrange the following alcohols **(a)** in the decreasing order of their boiling points and **(b)** in the decreasing order of their solubility in water.

(1) *n*-Butyl alcohol

(2) *sec*-Butyl alcohol and

(3) *tert*-Butyl alcohol

IV. Arrange the following compounds in the order of their increasing boiling points.

(1) CH_3COCl, **(2)** $(CH_3CO)_2O$, **(3)** CH_3CONH_2, **(4)** CH_3COOH

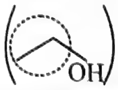
Sol.

I. (A) a. The decreasing order of boiling points is: Pentanol > Ethanol > Propane (3 > 1 > 2).

Pentanol and ethanol have H-bonding, but molecular mass of pentanol is more than ethanol, so it has high boiling point. Propane has the least boiling point due to non-polar character and weak van der Waals forces of attraction.

b. The decreasing order of solubility in H_2O is: Ethanol > Pentanol > Propane (1 > 3 > 2).

Both ethanol and pentanol have H-bonding, but non-

polar part  in pentanol is larger than non-polar part  in ethanol. So ethanol is more soluble in H_2O than pentanol. Propane is least soluble because of the non-polar character.

I.(B) a. The decreasing order of boiling point is:
1,2,3-Pentanetriol > Butyl alcohol > Butane (2 > 3 > 1). Due to three (OH) groups in compound (2), it has more H-bonding than in alcohol (3).

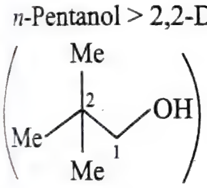
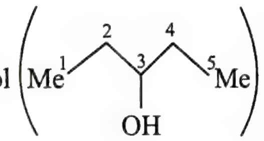
b. Decreasing solubility in H_2O: (2) > (3) > (1).
There is more H-bonding in compound (2) than in (3), hence it has more solubility in H_2O.

I.(C) a. The decreasing order of boiling point is:
Hexanol > Pentanol > Pentane (3 > 2 > 1)
Both alcohols have same H-bonding, but molecular mass of (3) > (2). Hence, the boiling point order is as given above.

b. The decreasing order of solubility in H_2O:
Pentanol > Hexanol > Pentane
[Same explanation as in I (A) (b) above.]

II.(A) The decreasing order of boiling point is:
$HOCH_2—CH_2OH > C_2H_5OH > (CH_3)_2O > C_3H_8$
(4 > 2 > 3 > 1)
(Same explanation as I (B) (a) above.)

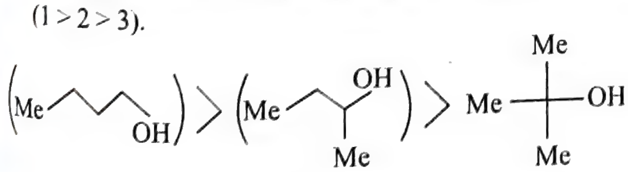
II.(B) The decreasing order of boiling points is:
n-Pentanol > 2,2-Dimethyl propanol


> 3-Pentanol


> *n*-Pentane (4 > 3 > 1 > 2)

Alcohols (4), (3) and (1) have H-bonding, but *n*-pentanol is a straight-chain compound and has a larger surface area, so the highest boiling point. Alcohol (3) is more sterically hindered than alcohol (1), hence it requires more energy to boil off. Therefore, boiling point of alcohol (3) > alcohol (1).

III. a. The decreasing order of boiling points is:
n-Butyl alcohol > *sec*-Butyl alcohol > *t*-Butyl alcohol (1 > 2 > 3).



All alcohols have H-bonding, but alcohol (1) has more surface area. Alcohol (2) has less surface area due to branching, and alcohol (3) has more branching and less surface area than in alcohol (2). Hence, the boiling point order is as given above.

b. Decreasing solubility order in H_2O:
t-Butyl alcochol > *sec*-Butyl alcohol > *n*-Butyl alcohol (3 > 2 > 1).

Lesser the surface area, greater is the solubility in H_2O. Hence, the solubility order is as given above.

IV. CH_3COOH undergoes intermolecular H-bonding while CH_3COCl does not. The boiling point of CH_3COOH is higher than that of CH_3COCl.

The molecular mass of $(CH_3CO)_2O$ is much higher than that of CH_3COOH. As a result, $(CH_3CO)_2O$ has a higher boiling point than that of CH_3COOH due to stronger van der Waals forces of attraction. Like CH_3COOH, CH_3CONH_2 also forms intermolecular H-bonds, whereas in CH_3COOH only cyclic dimers are formed. In CH_3CONH_2, intermolecular H-bonds lead to the association of a number of molecules. As a result, the boiling point of CH_3CONH_2 is much higher than that of CH_3COOH. Further, this higher degree of association of CH_3CONH_2 molecules compensates for the effect of increased molecular size of $(CH_3CO)_2O$. Consequently, boiling point of CH_3CONH_2 is even higher than that of $(CH_3CO)_2O$. In other words, the boiling points follow the sequence:

$CH_3COCl < CH_3COOH < (CH_3CO)_2O < CH_3CONH_2$

ILLUSTRATION 2.32

a. Arrange in decreasing order of melting and boiling points of hydrides of groups 15, 16 and 17.

b. Give the decreasing order of melting and boiling points of H_2O, NH_3 and HF.

c. Give the decreasing order of boiling points: (I) C_2H_5OH, (II) $(CH_3)_2NH$, (III) $C_2H_5NH_2$.

d. Give the decreasing order of solubility in H_2O. (I)$PhNH_2$, (II)$(C_2H_5)_2NH$, (III)$C_2H_5NH_2$.

Sol.

a. (Refer to Section 2.23.11, Points 2, 3 and 4.

i. Melting point of group 15 hydries: $NH_3 > BiH_3 > SbH_3 > AsH_3 > PH_3$.
Boiling point of group 15 hydries: $BiH_3 > SbH_3 > NH_3 > AsH_3 > PH_3$.

ii. Melting point of group 16 hydries: $H_2O > H_2Te > H_2Se > H_2S$.
Boiling point of group 16 hydries: $H_2O > H_2Te > H_2Se > H_2S$.

iii. Melting point of group 17 hydries: HI > HF > HBr > HCl.

Boiling point of group 17 hydries: HF > HI > HBr > HCl.

b. Refer to Section 2.23.11, Point 5.
Melting point: $H_2O > NH_3 > HF$.
Boiling point: $H_2O > HF > NH_3$.

c. i. Boiling point of alcohols > boiling points of amines (due to EN of O > EN of N)

ii. Boiling points of 1° amine > 2° amine > 3° amine due to three H-bonds, two H-bonds in 1° and 2° amines, 3° amine do not form H-bonds, since no H-atoms is present.

Therefore, decreasing boiling order is:

$C_2H_5OH > C_2H_5NH_2 > (C_2H_5)_2NH$ (I > III > II)

d. Solubility in H_2O of 1° amine > 2° amine > 3° amine due to three H-bonds and two H-bonds in 1° and 2° amines respectively. Aromatic amines are less soluble in H_2O due to larger non-polar part than aliphatic amines.

Therefore, decreasing solubility order is:

$C_2H_5NH_2 > (C_2H_5)_2NH : PhNH_2$ (III > II > I)

2.24 VALENCE BOND THEORY AND MOLECULAR ORBITAL THEORY

Limitations of valence bond theory (VBT): VBT does not explain satisfactorily the following.

1. The formation of chemical bond of molecules.
2. Their relative bond strength.
3. Their characteristic magnetic properties, i.e. paramagnetic and diamagnetic characters.
4. Their optical properties, i.e. colour of molecules in visible light.

To overcome the above limitations of VBT, another approach was developed by F. Hund and R.S. Mulliken in 1932, known as *molecular orbital theory* (MOT).

Salient features of MOT:

1. This theory suggests that when two atomic orbitals (AO) combine or overlap, they lose their identity and form new orbitals, which are known as molecular orbital (MO).

   Whereas in VBT, when two AO combine or overlap, they retain their identity.

   For example, the concept can be understood by taking two eggs opened in the same frying pan side by side [Fig. 2.67 (a)] in which yellow portion of both the eggs are seen separately while the white portion of both the eggs are mixed. This analogy represents the VB approach.

   When the two eggs are mixed thoroughly then white and yellow portions of both the eggs cannot be distinguished. This analogy represents the MO approach [Fig. 2.67 (b)].

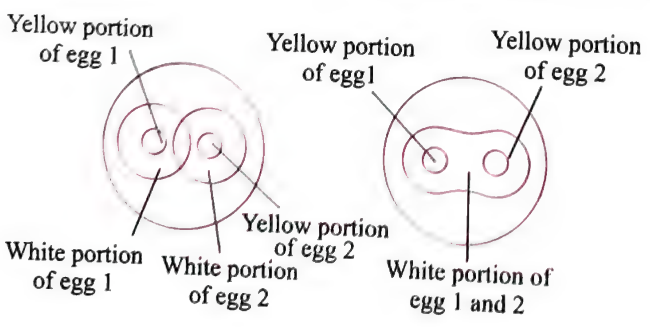


Fig. 2.67 (a) Analogy to distinguish between VB approach and (b) MO approach

VB approach and MO approach in terms of orbitals is represented as shown in Fig. 2.67 (c).

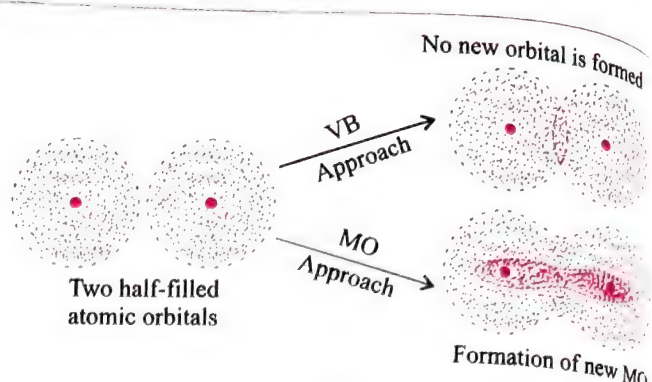


Fig. 2.67 (c) Difference in VB and MO approach

2. The electrons in a molecule are present in the various MO's as the electrons of atoms are present in the various AO's.
3. The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.

   For example, 1*s* can combine with 1*s* and not with 2*s*; similarly, *s*-orbital can overlap (combine) with p_z but not with p_x or p_y.

   Likewise p_z can combine with p_z but not with p_x or p_y. By convention Z-axis is taken as the internuclear or molecular axis.
4. While an electron in an AO is influenced by one nucleus, in a MO it is influenced by two of more nuclei depending upon the number of atoms in the molecule. Thus, an AO is monocentric while a MO is polycentric.
5. The number of MO formed is equal to the number of combining AO's. When two AO's combine, two MO's are formed. One is known as **bonding molecular orbital** while the other is called **antibonding molecular orbital.**
6. The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital (ABMO).
7. Just as the electron probability distribution around a nucleus in an atom is given by an AO, the electron probability distribution around a group of nuclei in a molecule is given by a MO.
8. The MO's like AO's are filled in accordance with the *Aufbau principle* obeying the *Pauli exculsion principle* and the *Hund's rule.*
9. The bonding MO's are represented by σ, π, δ etc. whereas the corresponding antibonding MO's are represented by σ^*, π^*, δ^* etc.

2.24.1 COMPARISON BETWEEN AO'S AND MO'S

The comparison between AO's and MO's is given in Table 2.16.

Table 2.16 Comparison between AO's and MO's

AO's	MO's
1. Their electron cloud extends around the nucleus of a single atom, i.e. AO is monocentric.	1. Their electron cloud extends around all the nuclei of bonded atoms in the molecule, i.e. a MO is polycentric. They are obtained by combining AO's of comparable energy.
2. They have simple shapes.	2. They have complex shapes.
3. They are represented by *s*, *p*, *d*, *f* etc.	3. They are represented by σ, σ*, π, π*, etc. They may be bonding or antibonding.
4. They are less stable.	4. They are more stable.

2.24.2 Formation of Molecular Orbitals by Linear Combination of Atomic Orbitals

According to wave mechanics, the AO's can be expressed by wave functions (ψ's) which represent the amplitude of the electron waves. These are obtained from the solution of Schrödinger wave equation. However, since it cannot be solved for any system containing more than one electron, MO's which are one electron wave functions for molecules are difficult to obtain directly from the solution of Schrödinger wave equation. To overcome this problem, an approximate method known as linear combination of atomic orbitals (LCAO) has been adopted.

According to the principle of LCAO, an atomic orbital is an electron wave. The waves of the two AO's may be in phase or out of phase (Fig. 2.68).

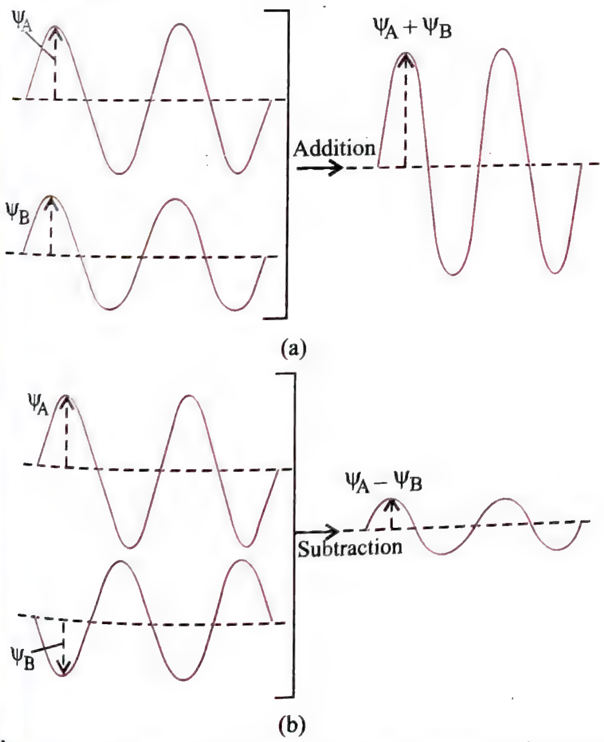


Fig. 2.68 (a) Additive effect of the electron waves in phase and (b) Subtractive effect of the electron waves out of phase

Suppose ψ_A and ψ_B represent the amplitude (or also called the *wave functions*) of the electron waves of the atomic orbitals of the two atoms A and B respectively, then the situation may be represented as follows:

1. When the two waves are in phase (constructive interference) so that they add up and the amplitude of the new wave is
$$\sigma = \psi_A + \psi_B$$
2. When the two waves are out of phase (destructive interference), the waves are subtracted from each other so that the amplitude of the new wave is
$$\sigma^* = \psi_A - \psi_B$$
Knowing that the probability is given by the square of the amplitude, we have
$$\sigma^2 = (\psi_A + \psi_B)^2 = \psi^2_A + \psi^2_B + 2\psi_A\psi_B$$
and $$\sigma^{*2} = (\psi_A - \psi_B)^2 = \psi^2_A + \psi^2_B - 2\psi_A\psi_B.$$
i.e. $\sigma^2 > \psi^2_A + \psi^2_B$
whereas $\sigma^{*2} < \psi^2_A + \psi^2_B$
   a. Thus, by combination of two AO's, two new MO's (σ and σ*) are formed, one by additive effect and the other by the subtractive effect of the AO's.
   b. The MO (σ) formed by the additive effect of the A.O's is called *bonding molecular orbital.*
   c. The MO (σ*) formed by the subtractive effect of the AO's is called *antibonding* molecular orbital as shown in Fig. 2.69.

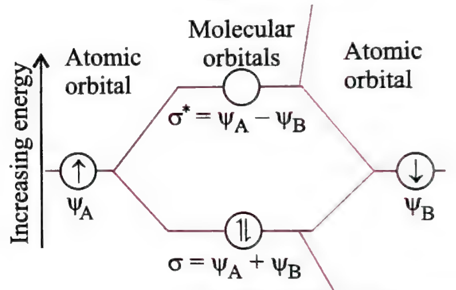


Fig. 2.69 Formation of bonding (σ) and antibonding (σ*) molecular orbitals by the linear combination of atomic orbitals ψ_A and ψ_B centred on two atoms A and B respectively

Qualitatively, the formation of molecular orbitals can be understood in terms of the constructive or destructive interference of the electron waves of the combining atoms. In the formation of bonding molecular orbital, the two electron waves of the bonding atoms reinforce each other due to constructive interference while in the formation of antibonding MO, the electron waves cancel each other due to destructive interference.

Just as atomic orbitals are represented by s, p, d etc., the bonding molecular orbitals are represented by σ, π, δ etc., and the corresponding antibonding molecular orbitals are represented by putting an asterisk, i.e. by σ*, π*, δ* etc.

It may be pointed out here that the crests of the electron wave are usually given a '+' sign and the troughs a '–' sign (Fig. 2.70). Thus, bonding molecular orbital is formed by the combination of '+' with '+' and '–' with '–' part of the electron waves, whereas antibonding MO's are formed by the overlap of '+' with '–' part. However, these '+' and '–' signs have nothing to do with

the electrical charges on the orbitals. They simply represent the sign of the wave function.

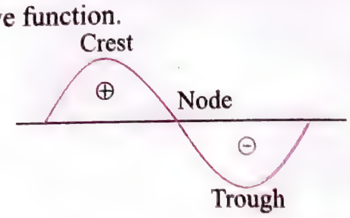


Fig. 2.70 Sign convention in an electron wave

d. The electron density in a bonding MO is located between the nuclei of the bonded atoms and hence repulsion between both the nuclei is very less or attraction between both the nuclei is very strong.

In other words, the probability of finding the electrons in the bonding MO increases.

e. In case of an antibonding MO, most of the electron density is located away from the space between the nuclei and hence repulsion between both the nuclei is very high or attraction between both the nuceli is very less.

In other words, the probability of finding the electrons in the antibonding MO decreases.

Nodal plane is that on which the electron density is zero.

In fact, there is a nodal plane between the nuclei and hence the repulsion between the nuclei is high.

f. Electrons in a bonding MO tend to hold the nuclei together and stabilise a molecule.

Therefore, a bonding MO always have lower energy than either of the AO's, that have combined to form it.

g. Electrons in a antibonding MO destabilise the molecule. Because of mutual repulsion of the electrons in this orbital is more than the attraction between the electrons and the nuclei. Hence, the net energy is increased.

h. Energy of bonding MO is lowered than the energy of the parent AO's that have combined.

Whereas the energy of antibonding MO is raised above the parent AO's that have combined.

The total energy of two MO's however remains the same as that of two original AO's as shown in Fig. 2.71.

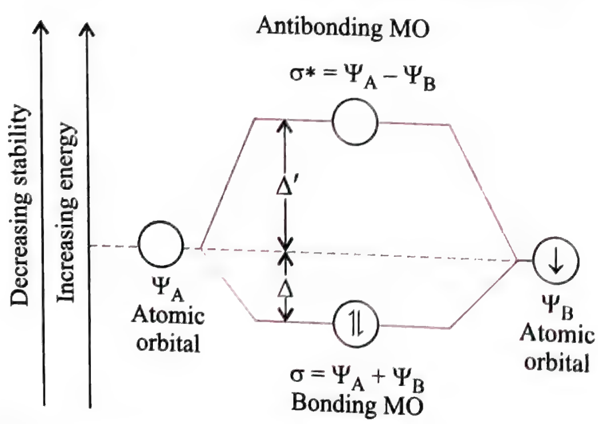


Fig. 2.71 Formation of bonding and antibonding molecular orbitals

The lowering of energy (Δ) of the bonding MO than the combining AO is called the *stabilisation energy* while increase in energy (Δ') of the antibonding MO is called the *destabilisation energy*.

2.24.3 Conditions for the Combination of Atomic Orbitals

LCAO's to form molecular orbitals take place only if the following conditions are satisfied:

1. **The combining atomic orbitals must have the same or nearly the same energy.** This means that 1*s* orbital can combine with another 1*s* orbital but not with 2*s* orbital because the energy of 2*s* orbital is appreciably higher than that of 1*s* orbital. **This is not true if the atoms are very different.**
2. **The combining atomic orbitals must have the same symmetry about the molecular axis.** By convention Z-axis is taken as the molecular axis. The atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. For example, $2p_z$ orbital of one atom can combine with $2p_z$ orbital of the other but not with the $2p_x$ or $2p_y$ orbitals because of their different symmetries [Figs. 2.72(a) and (b)].
3. **The combining atomic orbitals must overlap to the maximum extent.** Greater the extent of overlap, the greater will be the electron density between the nuclei of a molecular orbital.

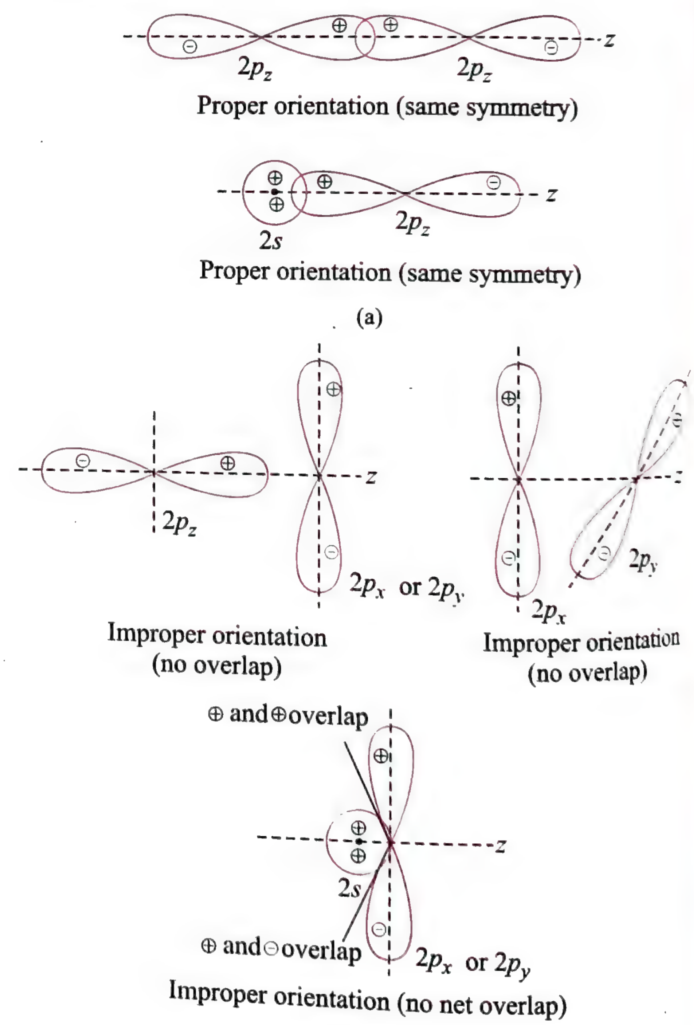


Fig. 2.72 (a) Proper orientation of overlap (b) Improper orientation of overlap

2.24.4 Types of Molecular Orbitals

Molecular orbitals of diatomic molecules are designated as σ (sigma), π (pi), δ (delta) etc.

If two AO's overlap along the internuclear axis, the MO formed is called σ MO and they are symmetrical around the bond axis.

If two AO's overlap sideways, the MO formed is called π MO and they are not symmetrical around the internuclear axis.

Note: The different orbitals in terms of signs of wave function are represented as:

i. Since *s*-orbital is spherical symmetrical, their wave function has the same sign in all direction.

ii. Since *p*-orbital has two lobes, so one lobe is given a ⊕ sign and other a ⊖ sign.

iii. Formation of the bonding MO is represented by the overlapping of ⊕ part of the electron cloud of one atom with ⊕ part of the electron cloud of the second atom or ⊖ part with ⊖ part.

iv. In Fig. 2.72 (b), the combination of $2s - 2p_x$, there is a small overlapping. The area of (+) (+) overlap is equal to the area of (+) (–) overlap. Therefore, the two areas are equal but opposite in signs. Hence, they cancel out.

v. Formation of the antibonding MO is represented by the overlapping of ⊕ part of the electron cloud of one atom with ⊖ part of the electron cloud of the second atom or ⊖ part with ⊕ part.

1. **Overlap of 1s with 1s:** The wave function of two 1*s* orbitals can combine in two different ways:
   a. When both have same wave phases (or function), i.e. both have same sign.
   b. When both have different wave phases (or function), i.e. both have different signs.

   If one of the wave functions is arbitrarily assigned a +ve sign, the other may be either +ve or –ve. The bonding molecular orbital formed is designated as σ (1*s*), σ indicating that the overlap is along the internuclear axis and 1*s* indicating that 1*s* atomic orbitals have combined to form the MO. The corresponding antibonding molecular orbital is designated as σ* (1*s*) (Fig. 2.73).

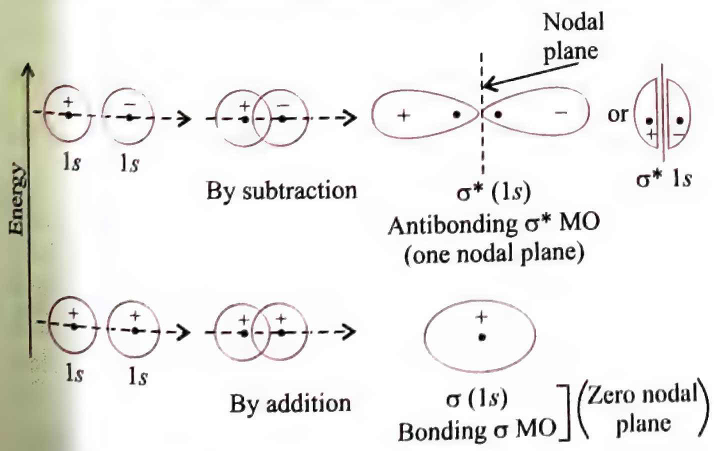


Fig. 2.73 Contours and energies of bonding and antibonding orbitals formed through combination of 1s AO's

2. **Overlap of 2s with 2s:** This type of overlap takes place exactly in the same manner as between 1*s* with 1*s* but in this case bonding and antibonding M.O are represented as σ (2*s*) and σ* (2*s*) respectively.

3. **Overlap of $2p_z$ with $2p_z$:** The bonding and antibonding MO's formed are as shown in Fig. 2.74.

Note: Z-axis is chosen arbitrarily as the internuclear axis.

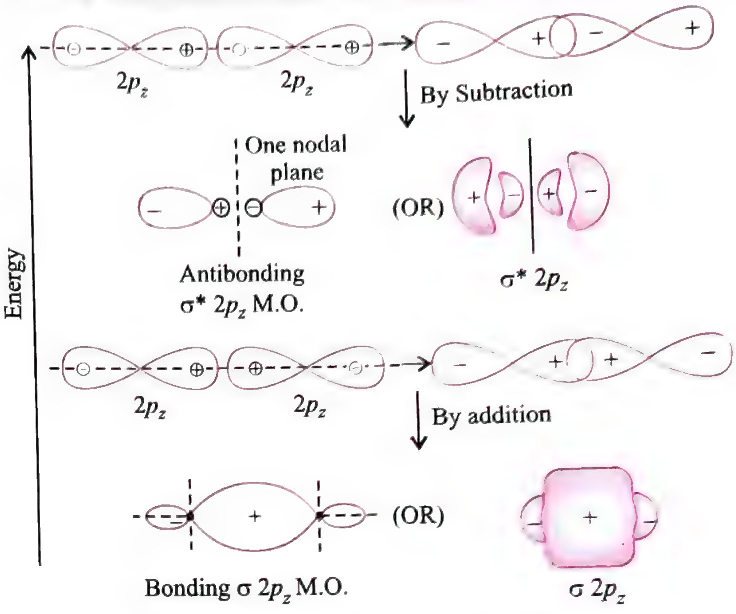


Fig. 2.74 Combination of two $2p_z$ AO's to form σ $(2p_z)$ and σ* $(2p_z)$ MO's

Note: σ $2p_z$ MO. have two and σ* $2p_z$ M.O has one nodal plane respectively.

4. **Overlap of $2p_x$ with $2p_x$ or $2p_y$ with $2p_y$:** The bonding and antibonding MO's formed are as shown in Fig. 2.75.

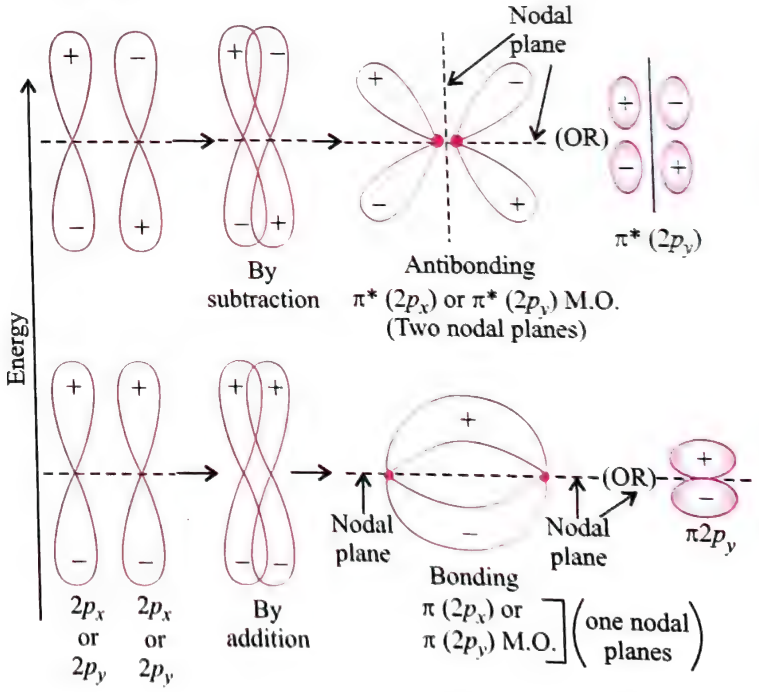


Fig. 2.75 Combination of two $(2p_x)$ or two $2p_y$ AO's to form π $(2p_x)$ and π*$(2p_x)$ or π $(2p_y)$ and π* $(2p_y)$ MO's

Note: i. In this case, bonding MO formed, i.e. π $(2p_x)$ or π $(2p_y)$ in which π indicates sideway overlap.

ii. π $(2p_x)$ or π $(2p_y)$ has one nodal plane.

iii. π* $(2p_x)$ or π* $(2p_y)$ has two nodal planes.

2.24.5 Comparison Between Bonding and Antibonding MO's

The main points of difference are summed up as below.

Bonding molecular orbitals	Antibonding molecular orbitals
1. They are formed by the additive effect of the AO's $\sigma = \psi_A + \psi_B$	1. They are formed by the subtractive effect of the AO's $\sigma^* = \psi_A - \psi_B$
2. The electron density increases in the region between the nuclei of bonded atoms.	2. The electron density decreases in the region between the nuclei of the atoms and it increases in the region away from the internuclear region. This is responsible for the instability of the bond.
3. The electrons present in the bonding orbitals result in the attraction between the two atoms.	3. The electrons present in the antibonding MO's (if any) result in the repulsion between the two atoms.
4. Because of attractive forces involved, these MO's have lower energy than the AO's from which they are formed. This is the cause of their stability.	4. Because of the repulsive forces involved, these MO's have higher energy than the AO's from which they are formed. This is the cause of their lower stability, i.e. it does not favour bond formation and that is why the name antibonding.
5. They are formed when the lobes of the combining orbitals have the same sign.	5. They are formed when the lobes of the combining orbitals are of opposite sign.
6. These MO's are represented by σ and π.	6. These MO's are represented by σ^* and π^*.

2.24.6 Comparison Between σ and π MO's

The main points of difference are summed up as below.

σ - Molecular Orbital	π-Molecular Orbital
1. It is formed by the overlap of AO's along the internuclear axis.	1. It is formed by the sideway overlaping of the AO's.
2. It consists of one electron cloud.	2. It consists of two electron clouds, one lying above and the other lying below a plane passing through the nuclei.
3. Due to head on overlap, the overlapping is maximum.	3. Due to sideway overlap, the overlapping is less:
4. Its electron cloud is symmetrical about the internuclear axis.	4. Its electron cloud is not symmetrical about the internuclear axis.

2.24.7 Energy Level Diagram for MO's

It may be noted that $1s$ AO's on two atoms form two MO's designated as σ $1s$ and σ^* $1s$. In the same manner, the $2s$ and $2p$ AO's (8 AO's on 2 atoms) give rise to the following 8 MO's.

Anitibonding MO's	σ^* $2s$, σ^* $2p_z$, π^* $2p_x$, π^* $2p_y$
Bonding MO's	σ $2s$, σ $2p_z$, π $2p_x$, π $2p_y$

The energy levels of these MO's have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of 2nd period of the periodic table. The increasing order of various molecular orbitals for O_2 and F_2 is given below [Fig. 2.76 (a)].

σ $1s$ < σ^* $1s$ < σ $2s$ < σ^*2s < $\sigma 2p_z$ < $(\pi 2p_x \equiv \pi\ 2p_y)$ < $(\pi\ ^*2p_x \equiv \pi\ ^*2p_y) < \sigma\ ^*2p_z$.

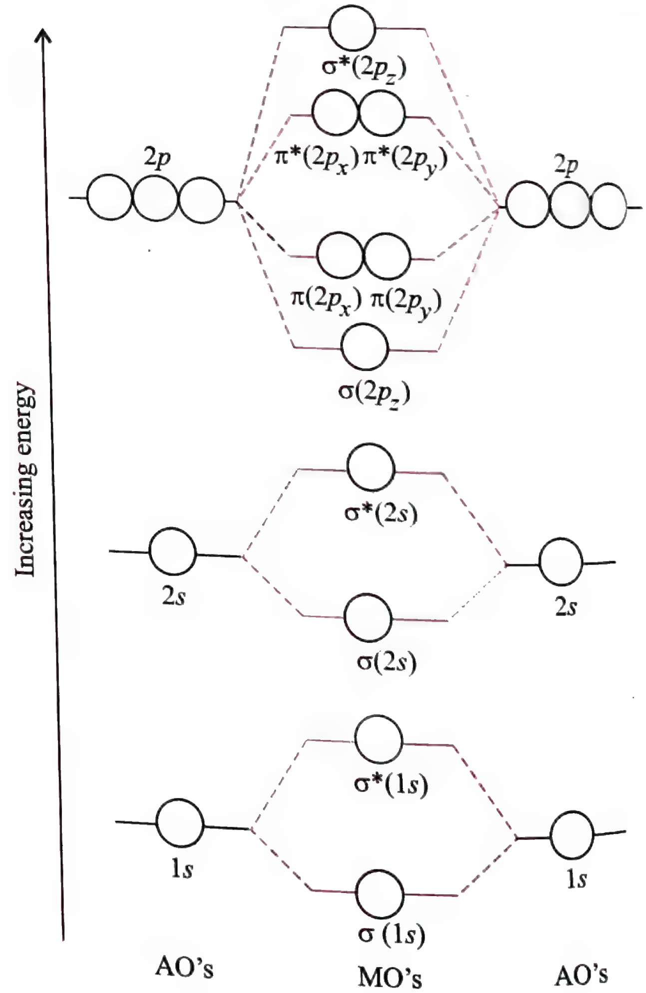
However, this sequence of energy levels of molecular orbitals is not correct for the remaining orbitals is not correct for the remaining molecules Li_2, Be_2, B_2, C_2, N_2. For instance, it has been observed experimentally that for molecules such as B_2, C_2, N_2 etc. the increasing order of energies of various molecular orbitals is as follows (Fig. 2.76 b).

σ $1s$ < σ^* $1s$ < σ $2s$ < σ^*2s $(\pi 2p_x \equiv \pi\ 2p_y) < \sigma 2p_z < (\pi\ ^*2p_x \equiv \pi\ ^*2p_y) < \sigma\ ^*2p_z$.

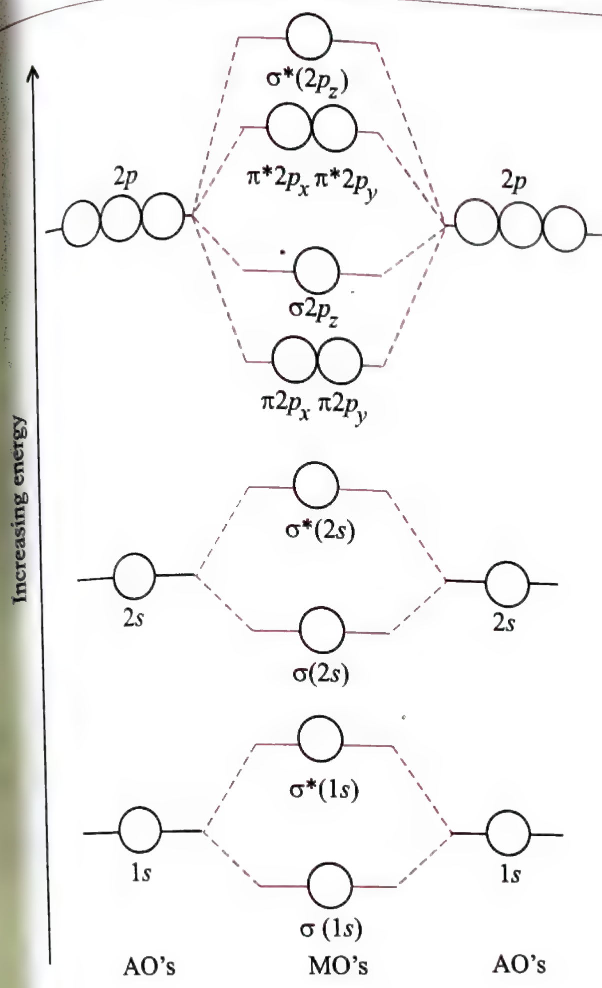
The important characteristic feature of this order is that the energy of $\sigma 2p_z$ molecular orbital is higher than that of $\sigma 2p_x$ and σ^*2p_y molecular orbitals.

2.24.8 Explanation for Different MO Energy Level Diagrams

It would be expected that σ $(2p)$ orbital would be of lower energy than a comparable π $(2p)$ orbital because σ-bonds are generally stronger. However, for most of the elements, σ $(2p)$ orbital lies at a higher energy than π $(2p)$ orbitals becuase the difference



(a)



(b)

Fig. 2.76 (a) MO's energy level diagram for O_2, F_2 and Ne_2 (i.e. with Z > 7). (b) MO's energy level diagram for H_2, C_2, and N_2 (i.e. with Z ≤ 7)

between 2s and 2p atomic energy levels is small (except in case of O_2 and F_2 where the difference in energy levels of 2s and 2p is large). As a result, σ (2s) and σ (2p) are so close together that the repulsive forces between the electrons present in them raise the energy of σ (2p) above that of π (2p) MO's.

Difference in energy splitting of σ_{2p} and π_{2p} orbitals: The energy splitting between bonding and antibonding orbitals is larger for σ_{2p} orbitals than it is for π_{2p} orbitals, because the overlap of p orbitals is greater when they are oriented along the axis to form σ-orbitals than when they are oriented to overlap sideways to form π orbitals.

2.24.9 Electronic Configuration and Molecular Behaviour

The distribution of electrons among various molecular orbitals is called the **electronic configuration of the molecule**. From the electronic configuration of the molecule, it is possible to get important information about the molecule as discussed below.

Stability of molecules: If N_b is the number of electrons occupying bonding orbitals and N_a the number occupying the antibonding orbitals, then

1. The molecule is stable if N_b is greater than N_a, and
2. The molecule is unstable if N_b is less than N_a.

In (1), more bonding orbitals are occupied and so the bonding influence is stronger and a stable molecule results. In (2), the antibonding influence is stronger and therefore the molecule is unstable.

2.24.9.1 Bond Order

Bond order (BO) is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals, i.e.

$$BO = \frac{1}{2}(N_b - N_a)$$

The rules discussed above regarding the stability of the molecule can be restated in terms of bond order as follows. A positive bond order (i.e. $N_b > N_a$) means a stable molecule while a negative (i.e. $N_b < N_a$) or zero (i.e. $N_b = N_a$) bond order means an unstable molecule. Bond order of + ½ indicates that the species exits but is unstable, e.g. $H_2^{\oplus}$ and $He_2^{\oplus}$.

2.24.9.2 Nature of the Bond

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds, respectively, as studies in the classical concept. Bond order may be fractional and even zero.

2.24.9.3 Bond Length

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length (BL). The bond length decreases as bond order increases.

$$BO \propto \Delta_{BE} H^{\ominus} \text{ and } BO \propto \frac{1}{\text{Bond length}}$$

Molecule	BO	BL	$\Delta_{BE}.H^{\ominus}$ kJ mol^{-1}
F_2 (F – F)	1	142 pm	158
O_2 (O = O)	2	121 pm	498
N_2 (N ≡ N)	3	110 pm	945

Magnetic nature: If all the MO's in a molecule are paired, the substance is diamagnetic (repelled by magnetic field). However, if one or more MO's are unpaired, it is paramagnetic (attracted by magnetic field), e.g. O_2 molecule.

Magnetic moment (μ_{MM}) = $\sqrt{n(n+2)}$ BM

where n is the number of unpaired e^-'s.

2.24.10 Bonding in Some Homonuclear Diatomic Molecules/Ions of Periods 1 and 2

The filling of MO's takes place according to the following principles:

1. The filling of MO's occurs according to the same principle as applicable to filling of AO's, i.e. Aufbau principle (MO's are filled in order of their increasing energies).
2. According to Pauli exclusion principle, a MO can have a maximum of two electrons and these must have opposite spins.
3. According to Hund's rule of maximum multiplicity, pairing of electrons in degenerate MO's does not take place until each one of them has one electron with the same spin.

Note: The shapes of MO's formed depend upon the type of combining AO's.

2.24.10.1 Examples of Bonding in Some Homonuclear Diatomic Molecules/Ions

1. **Hydrogen molecule (H_2):** It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in $1s$ orbital. Therefore, in all there are two electrons in hydrogen molecule which are present in σ $1s$ molecular orbital. So, electronic configuration of hydrogen molecule is H_2: $(\sigma\ 1s)^2$. The bond order of H_2 molecule can be calculated as given below:

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

a. **Stability:** This means that the two hydrogen atoms are bonded together by a single covalent bond. The bond dissociation energy of hydrogen molecule has been found to be 438 kJ mol^{-1} and bond length equal to 74 pm.

b. **Diamagnetic character:** Since no unpaired electron is present in H_2 molecule, therefore it is *diamagnetic.*

c. Energy level diagram is represented as shown in Fig. 2.77.

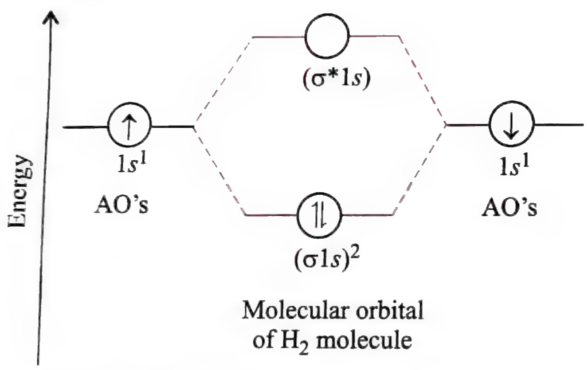


Fig. 2.77 Energy level diagram of H_2 molecule

2. **Hydrogen molecule positive ion ($H_2^{\oplus}$):**

a. $H\ (Z = 1) \Rightarrow 1s^1$

Total number of electrons in $H_2^{\oplus}$ ion $= 1 + 1 - 1 = 1$

b. The electronic configuration of $H_2^{\oplus}$ ion $= (\sigma\ 1s)^1$

c. Bond order (BO) $= \frac{1}{2}\ (N_b - N_a) = \frac{1}{2}\ (1-0) = 1$

d. Energy level diagram is represented as shown in Fig. 2.78.

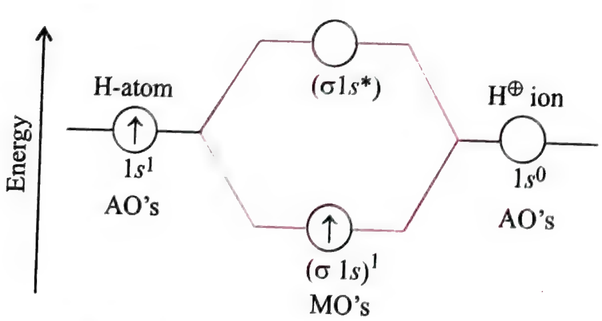


Fig. 2.78. MO energy level diagram for $H_2^{\oplus}$ ion

e. **Stability:** $H_2^{\oplus}$ ion should be stable, since the BO is positive. But the stability is not very high due to low value of BO.

f. **Paramagnetic character:** Since one unpaired electron is present in $H_2^{\oplus}$ ion, therefore it is paramagnetic.

$$\mu_{mm} = \sqrt{n\,(n+2)}\ \text{BM}$$
$$= \sqrt{1\,(1+2)} = \sqrt{3}\ \text{BM}$$

g. $H_2^{\oplus}$ ion is the simplest molecular species containing one electron only. Its existence has been detected spectroscopically when an electric discharge is passed through a discharge tube containing H_2 gas at low pressure.

3. **Hydrogen molecule negative ion ($H_2^{\ominus}$):**

a. $H\ (Z = 1) \Rightarrow 1s^1$

Total number of electrons in $H_2^{\ominus}$ ion $= 1 + 1 + 1 = 3$

b. The electronic configuration of $H_2^{\ominus}$ ion $= (\sigma\ 1s)^2, (\sigma^*\ 1s)^1$

c. Bond order (BO) $= \frac{1}{2}\ (2-1) = \frac{1}{2}$

According to Aufbau and Pauli exclusion principle, three electrons are filled in M.O's as shown in energy level diagram (Fig. 2.79).

d. Energy level diagram is represented as shown in Fig. 2.79.

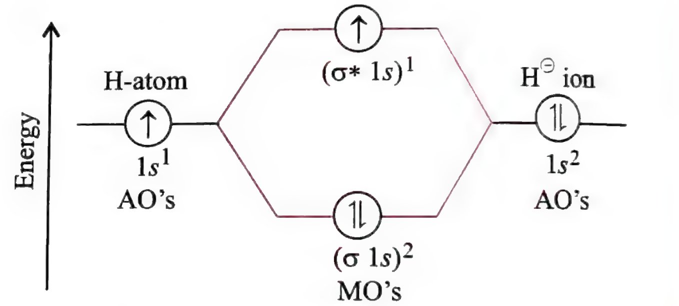


Fig. 2.79 MO energy level diagram for $H_2^{\ominus}$ ion.

e. $H_2^{\ominus}$ ion is somewhat stable due to smaller positive value of BO.

f. **Paramagnetic character:** Since one unpaired electron is present in $\sigma^*\ (1s)$ orbital, therefore it is paramagnetic.

$$\mu_{mm} = \sqrt{n\,(n+2)} = \sqrt{1\,(1+2)}$$
$$= \sqrt{3}\ \text{BM}$$

g. **Comparison between the stabilities of $H_2^{\oplus}$ and $H_2^{\ominus}$ ions:**

i. More the number of electrons in bonding MO's, more stable is the species.

ii. More the number of electrons in antibonding MO's, less stable is the species.

Although BO of $H_2^{\oplus}$ and $H_2^{\ominus}$ is same (i.e. 1/2) yet $H_2^{\oplus}$ is slightly more stable than $H_2^{\ominus}$, because $H_2^{\ominus}$ contains one electron in the antibonding MO which results in repulsion and decreases the stability.

Whereas $H_2^{\oplus}$ does not have any electron in the antibonding MO, so it is more stable.

Decreasing order of stabilities of H_2, $H_2^{\oplus}$ and $H_2^{\ominus}$ is as below:

$H_2 > H_2^{\oplus} > H_2^{\ominus}$

4. Helium molecule (He_2):

a. He (Z = 2) $1s^2$

Total number of electrons in He_2 molecule = 2 + 2 = 4

b. The electronic configuration of $He_2 = (\sigma\ 1s^2)\ (\sigma^*\ 1s)^2$

$BO = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2-2) = 0$

c. No bond is formed between two He atoms so He_2 molecule does not exist.

d. Energy level diagram is represented as shown in Fig. 2.80.

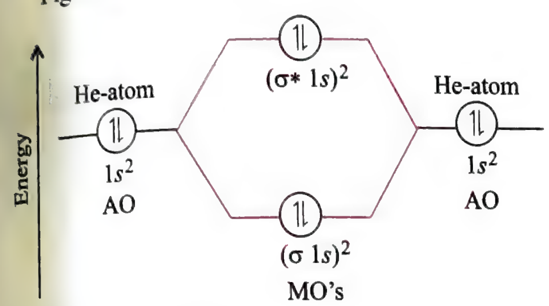


Fig. 2.80 MO energy level diagram for He_2 molecule

5. Helium molecule positive ion ($He_2^{\oplus}$):

a. Total number of electrons in $He_2^{\oplus}$ = 2 + 2 − 1 = 3

b. The electronic configuration of $He_2^{\oplus} = (\sigma\ 1s)^2, (\sigma^*\ 1s)^1$

c. $BO = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2-1) = \frac{1}{2}$

d. Energy level diagram is represented as shown in Fig. 2.81.

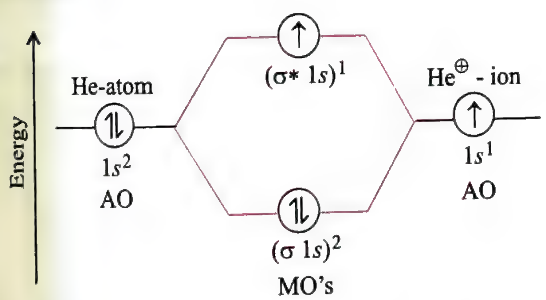


Fig. 2.81 MO energy level diagram for $He_2^{\oplus}$ ion

e. Characteristics of $H_2^{\ominus}$ and $He_2^{\oplus}$ ions:

i. Both have same BO.

ii. Both have same number of electrons in antibonding MO.

iii. Thus, both of them have similar stability, similar bond dissociation energy, similar bond length (BL) and paramagnetic character. These data are verified by experiments.

6. Beryllium molecule (Be_2):

a. Be (Z = 4) ⇒ $1s^2\ 2s^2$

Total number of electrons in Be_2 molecule = 4 + 4 = 8

b. The electronic configuration of Be_2:

$(\sigma\ 1s)^2\ (\sigma^*\ 1s)^2, (\sigma\ 2s)^2\ (\sigma^*\ 2s)^2$

c. Like He_2 molecule, Be_2 molecule also does not exist, since both have zero bond order.

7. Lithium molecule (Li_2):

a. Li (Z = 3) ⇒ $1s^2\ 2s^1$

Total number of electrons in Li_2 molecule = 3 + 3 = 6

b. The electronic configuration of Li_2 molecule is:

$(\sigma\ 1s)^2\ (\sigma^*\ 1s)^2\ (\sigma\ 2s)^2$ or $KK^*\ (\sigma\ 2s)^2$

Note: i. The above configuration is also written as KK^* $(\sigma\ 2s)^2$, where KK^* represents the closed K shell structure.

K indicates first bonding MO and K^* indicates first antibonding MO.

Thus, KK^* is same as $(\sigma\ 1s)^2\ (\sigma^*\ 1s)^2$.

ii. These KK^* (closed K shell) are omitted in the energy diagram.

c. $BO = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(4-2) = 1$

d. This shows that Li_2 is a stable molecule.

e. Energy level diagram is represented as shown in Fig. 2.82.

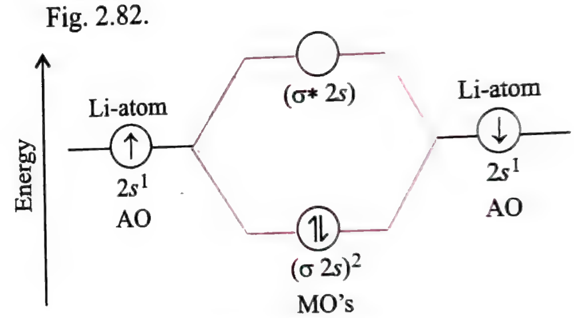


Fig. 2.82 MO energy level diagram for Li_2 molecule

f. **Diamagnetic character:** Since it has no unpaired electron, so it is diamagnetic, indeed diamagnetic Li_2 molecules are known to exist in the vapour phase.

8. Comparison between the stabilities of H_2, Li_2 and B_2 molecules:

a. Although bond order of H_2, Li_2 and B_2 is same (i.e. one), yet they are not equally stable.

Size of Li atom > size of H-atom.

Therefore, bond length of Li–Li (265 pm) > bond length of H – H (74 pm).

Moreover, there are 2 e^-'s in the antibonding MO $(\sigma^*\ 1s^2)$ of Li_2 whereas there is no electron in the antibonding MO of H_2.

Therefore, stability of H_2 > stability of Li_2. Bond energy of H_2 (438 kJ mol^{-1}) is greater than bond energy of Li_2 (110 kJ mol^{-1}).

b. Size of Li atom > size of B-atom

Therefore, bond length of Li–Li (265 pm) > bond length of B–B (159 pm).

Electronic configuration of B (Z = 5) ⇒ $1s^2 2s^2 2p^1$

Electronic configuration of B_2 molecule is:

$KK^* (\sigma\ 2s)^2 (\sigma^*\ 2s)^2 (\pi\ 2p_x^1 = \pi\ 2p_y^1)$

Moreover, there are two e^-'s more in the bonding MO's of B_2 than Li_2.

Hence, B_2 is more stable than Li_2 but less stable than H_2.

Therefore, bond energy (BE) of H_2 (438 kJ mol^{-1}) > BE of B_2 (290 kJ mol^{-1}) > BE of Li_2 (110 kJ mol^{-1}).

Thus, the order of stability is: $H_2 > B_2 > Li_2$.

9. **Carbon molecule (C_2):**

a. C (Z = 6) $\Rightarrow 1s^2 2s^2 2p^2$

Total number of electrons in C_2 molecule = 6 + 6 = 12

b. The electronic configuration of C_2 molecule is:

$(\sigma\ 1s)^2 (\sigma^*\ 1s)^2 (\sigma\ 2s)^2 (\sigma^*\ 2s)^2 (\pi\ 2p_x^2 \equiv \pi\ 2p_y^2)$

(OR) $KK^* (\sigma\ 2s)^2 (\sigma^*2s)^2 (\pi\ 2p_x^2 \equiv \pi\ 2p_y^2)$

c. $BO = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8-4) = 2$

d. This shows that C_2 molecule is a stable molecule.

e. Energy level diagram is represented as shown in Fig. 2.83.

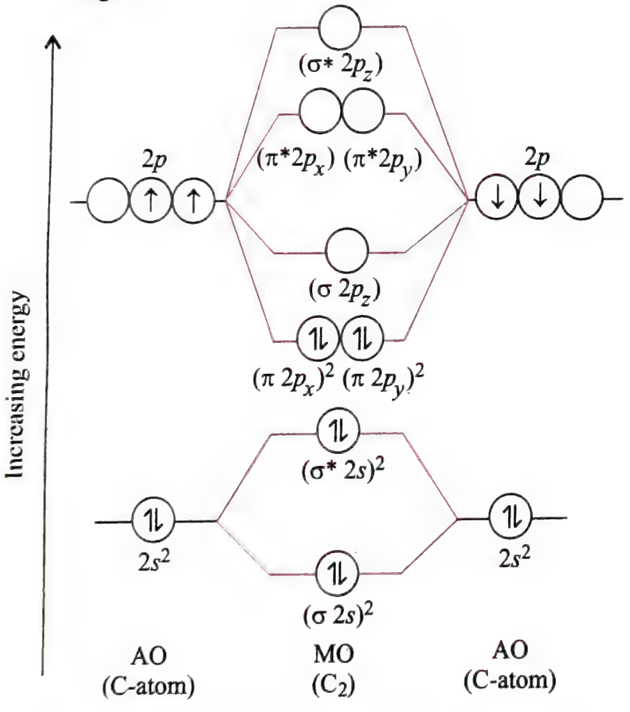


Fig. 2.83 M.O. energy level diagram for C_2 molecule

f. **Diamagnetic character:** Since it has no unpaired electrons, so it is diamagnetic. Diamagnetic C_2 molecules have indeed been detected in vapour phase.

Note: Double bond in C_2 consists of both pi (π) bonds because of the presence of four electrons in 2 π MO's.

While in most of the other molecules a double bond is made up of a σ and π bond.

g. It has been observed that like Li_2, C_2 molecules also exist in the vapour phase.

10. Comparison between the characteristics of Be_2, B_2 and C_2 molecules is given in Table 2.17.

Table 2.17 Characteristics of Be_2, B_2 and C_2 molecules

Molecule	Total number of e^-'s	Electronic configuration of molecules	Bond order	Magnetic character
Be_2	Be (Z = 4) 4 + 4 = 8	$KK^* (\sigma\ 2s)^2 (\sigma\ ^*2s)^2$	$\frac{1}{2}(2-2) = 0$	It does not exi[st]
B_2	B (Z = 5) 5 + 5 = 10	$KK^* (\sigma\ 2s)^2 (\sigma\ ^*2s)^2 (\pi\ 2p_x^1 \equiv \pi\ 2p_y^1)$	$\frac{1}{2}(4-2) = 1$	Paramagnetic
C_2	C (Z = 6) 6 + 6 = 12	$KK^* (\sigma\ 2s)^2 (\sigma^*\ 2s)^2 (\pi\ 2p_x^2 \equiv \pi\ 2p_y^2)$	$\frac{1}{2}(6-2) = 2$	Diamagnetic

Note:

1. Stability of C_2 > stability of B_2. Since the BO of C_2 > BO of B_2.
2. Number of bonding e^-'s in C_2 (i.e. 4 e^-'s) > Number of bonding e^-'s in B_2 (i.e. 2 e^-'s).

11. **Alternative method of calculation of bond order:** If the total number of e^-'s in the molecule/ ion ≥ 8. Then subtract 8 e^-'s from the total number of e^-'s. Since 8 e^-'s are counted for $(\sigma\ 1s)^2 (\sigma^*\ 1s)^2 (\sigma\ 2s)^2 (\sigma\ ^*2s^2)$.

Since the number of bonding and antibonding e^-'s are same up to 8 e^-'s in the molecule.

Case I (when Z ≤ 7): Remaining e^-'s will first enter into bonding $(\pi\ 2p_x \equiv \pi\ 2p_y)$ MO's and then into bonding $\sigma\ 2p_z$ MO's.

Case II (when Z ≥ 8): Remaining e^-'s will first enter into bonding $(\sigma\ 2p_z)$ MO and then into bonding $(\pi\ 2p_x \equiv \pi\ 2p_y)$

Examples :

a. **In case of N_2 molecule:**

Case I (when Z = 7)

Total e^-'s in N_2 = 7 + 7 = 14.

Remaining p e^-'s = 14 – 8 = 6.

So, four e^-'s will first enter into $(\pi\ 2p_x^2 \equiv \pi\ 2p_y^2)$ and two e^-'s will enter into $(\sigma\ 2p_z)^2$ MO's.

Antibonding MO does not have any electron.

Hence, $BO = \frac{1}{2}(6-0) = 3$

b. **In case of O_2 molecule:**

Case II (when Z = 8)

Total e^-'s in O_2 = 8 + 8 = 16

Remaining p e^-'s = 16 – 8 = 8

Therefore, six e^-'s will be in bonding and two e^-'s will be in antibonding MO's.

So, $BO = \frac{1}{2}(6-2) = 2$

But in this case two bonding e^-'s will enter into $(\sigma\ 2p_z)^2$ MO and then four bonding e^-'s will enter into $(\pi\ 2p_x^{\ 2} \equiv \pi\ 2p_y^{\ 2})$ MO's.

Remaining two antibonding e^-'s will enter into $(\pi^*\ 2p_x^{\ 1} \equiv \pi^*\ 2p^1_{\ y})$ according to Hund's rule.

Thus, two unpaired e^-'s are present in the antibonding MO and hence O_2 molecule is paramagnetic. Its magnetic moment (μ_{MM}) is:

$$\mu_{MM} = \sqrt{n\,(n+2)}\ \text{BM}$$
$$= \sqrt{2\,(2+2)} = \sqrt{8}\ \text{BM}$$

c. **In case of NO molecule:**

N (when Z = 7), O (when Z = 8)

Total e^-'s in NO = 7 + 8 = 15

Remaining p e^-'s = 15 – 8 = 7

Number of bonding e^-'s = 6

Number of antibonding e^-'s = 1

Thus,

$$\text{BO} = \frac{1}{2}(6-1) = 2.5$$

Since one unpaired e^- is present in the antibonding $(\pi^*\ 2p^1_{\ x})$ MO, therefore NO molecule is paramagnetic. Its magnetic moment (μ_{MM}) is:

$$\mu_{MM} = \sqrt{n\,(n+2)} = \sqrt{1\,(1+2)} = \sqrt{3}\ \text{BM}$$

12. **Nitrogen molecule (N_2):**

a. N (Z = 7) ⇒ $1s^2\ 2s^2,\ 2p^1_{\ x}\ 2p^1_{\ y}\ 2p^1_{\ z}$

Total number of e^-'s in N_2 molecule = 7 + 7 = 14

b. The electronic configuration of N_2 molecule is:

KK* $(\sigma\ 2s)^2\ (\sigma^*\ 2s)^2\ \ (\pi\ 2p^2_{\ x} \equiv \pi\ 2p^2_{\ y})\ (\sigma\ 2p_z)^2$

c. $\text{BO} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10-4) = 3$

Alternatively: Number of p e^-'s remaining after substracting eight e^-'s from total number of e^-'s = 14 – 8 = 6.

Number of bonding e^-'s = 6

Number of antibonding e^-'s = 0

Thus,

$$\text{BO} = \frac{1}{2}(6-0) = 3$$

d. **Nature of bond:** Since BO of N_2 is there, so it contains triple bond (N ≡ N).

e. **Bond strength:** Due to high BO value, N_2 has highest bond energy (945 kJ mol^{-1}) in comparison to other diatomic molecule.

f. Energy level diagram is represented as shown in Fig. 2.84.

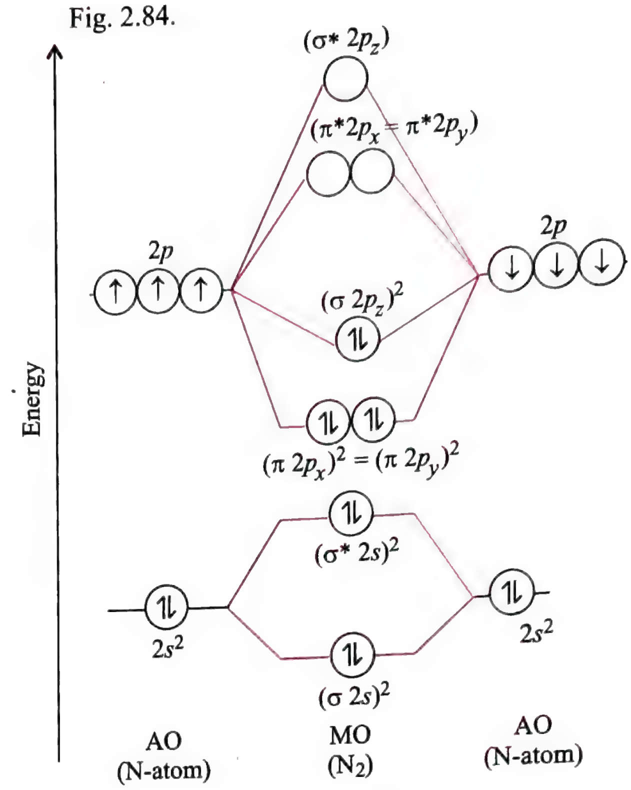


Fig. 2.84 MO energy level diagram for N_2 molecule

g. **Diamagnetic character:** Since it has no unpaired electrons, so it is diamagnetic.

h. **No. of σ and π bonds in N_2:**

$\pi = 2$ and $\sigma = 1$

4 e^-'s in $(\pi\ 2p_x)^2$ and $(\pi\ 2p_y)^2$ forms 2π bonds

2 e^-'s in $(\sigma\ 2p_z)^2$ forms 1σ bond.

13. **$N_2^{\oplus}$, $N_2^{\ominus}$ and $N_2^{\ 2-}$ ions:**

a. **$N_2^{\oplus}$ ion:**

i. $N_2^{\oplus}$ ion is formed by the loss of one e^- from $(\sigma\ 2p_z)$ MO of N_2 molecule.

ii. The electronic configuration of $N_2^{\oplus}$ ion is:

KK* $(\sigma^*\ 2s)^2\ (\pi\ 2p_x^{\ 2} \equiv \pi\ 2p_y^{\ 2})\ (\sigma\ 2p_z)^1$

iii. **Bond order:** Total e^-'s in $N_2^{\oplus}$ ion = 14 – 1 = 13

Remaining p e^-'s = 13 – 8 = 5

Number of bonding e^-'s = 5

Number of antibonding e^-'s = 0

$$\therefore\ \ \text{BO} = \frac{1}{2}(5-0) = 2.5$$

iv. **Paramagnetic charater:** $N_2^{\oplus}$ ion is paramagnetic in nature due to the presence of one unpaired e^- in $(\sigma\ 2p^1_{\ z})$ MO.

v. **No. of σ and π bonds in $N_2^{\oplus}$:** $\pi = 2$ and $\sigma = 0.5$

4 e^-'s in $(\pi\ 2p_x)^2$ and $(\pi\ 2p_y)^2$ forms 2π bonds

1 e^- $(\sigma\ 2p_z)^1$ forms 0.5σ bond.

b. $N_2^{\ominus}$ ion:

i. $N_2^{\ominus}$ ion is formed by the gain of one e^- by N_2 molecule. This e^- will enter into $\pi^* 2p_x$ or $\pi^* 2p_y$ antibonding MO's (Refer to Fig. 2.84).

ii. The electronic configuration of $N_2^{\ominus}$ ion is:

KK* $(\sigma\ 2s)^2\ (\sigma\ ^*2s)^2\ (\pi\ 2p^2_x \equiv \pi\ 2p_y^{\ 2})\ (\sigma\ 2p_z)^2\ (\pi^*2p_x^{\ 1})$.

iii. **Bond order:**

Total e^-'s in $N_2^{\ominus}$ ion $= 7 + 7 + 1 = 15$

Remaining $p\ e^-$'s $= 15 - 8 = 7$

Number of bonding e^-'s $= 6$

Number of antibonding e^-'s $= 1$

$\therefore\ \text{BO} = \frac{1}{2}(6-1) = 2.5$

iv. **Paramagnetic character:** $N_2^{\ominus}$ ion is paramagnetic in nature due to the presence of an unpaired e^- in $\pi^*\ 2p^1_x$ antibonding MO.

v. **No. of σ and π bonds in $N_2^{\ominus}$:** $\pi = 1.5$ and $\sigma = 1$

2 e^-'s in $(\pi\ 2p_x)^2$ and 1 e^- in ($\pi^*\ 2p_x$ or $\pi^* 2p_y$) forms 0.5 π bond

$2e^-$'s in $(\pi 2p_y)^2$ forms 1π bond.

Total $\pi = 0.5 + 1 = 1.5$

$2e^-$'s in $(\sigma\ 2p_z)^2$ forms 1π bond.

c. N_2^{2-} ion:

i. N_2^{2-} ion is formed by gain of two e^-'s by N_2 molecule. These two e^-'s will enter into $\pi^*\ 2p_x$ and $\pi^*\ 2p_y$ antibonding MO's one in each.

ii. The electronic configuration of N_2^{2-} ion is:

KK* $(\sigma\ 2s)^2\ (\sigma * 2s)^2\ (\pi\ 2p^2_x \equiv 2p^2_y)$
$(\sigma\ 2p_z)^2\ (\pi^*\ 2p_x)^1 \equiv (\pi^*\ 2p_y)^1$

iii. **Bond order:**

Total e^-'s in N_2^{2-} ion: $7 + 7 + 2 = 16$

Remaining $p\ e^-$'s $= 16 - 8 = 8$

Number of bonding e^-'s $= 6$

Number of antibonding e^-'s $= 2$

$\therefore\ \text{BO} = \frac{1}{2}(6-2) = 2$

iv. **Paramagnetic character:** N_2^{2-} ion is the paramagnetic due to presence of 2 unpaired e^-'s in $\pi^*\ 2p_x^{\ 1}$ and $\pi^*\ 2p_y^{\ 1}$. Its magnetic moment (μ_{MM}) is:

$$\mu_{MM} = \sqrt{n\,(n+2)}\ \text{BM}$$
$$= \sqrt{2\,(2+2)} = \sqrt{8}\ \text{BM}$$

v. **No. of σ and π bonds in N_2^{2-}:** $\pi = 1$ and $\sigma = 1$

$2e^-$'s in $(\pi\ 2p_x)^2$ and $1e^-$ in ($\pi^*\ 2p_x$ or $\pi^*\ 2p_y$) forms 0.5π bond

2 e^-'s in $(\pi\ 2p_y)^2$ and $1e^-$ in $(\pi^*\ 3p_y)$ forms 0.5π bond.

Total $\pi = 0.5 + 0.5 = 1$

$2e^-$'s in $(\sigma\ 2p_y)^2$ forms 1π bond.

14. Comparison of characteristics of N_2, $N_2^{\oplus}$, $N_2^{\ominus}$ and N_2^{2-} ions:

a. **Bond order:**

$N_2 = 3$, $N_2^{\oplus} = 2.5$, $N_2^{\ominus} = 2.5$, $N_2^{2-} = 2$

b. **Bond energy:**

Bond energy ∝ Bond order

Therefore, decreasing order of bond energies of these moleculear species is: $N_2 > N_2^{\oplus} = N_2^{\ominus} > N_2^{2-}$

c. **Bond length:**

$$\text{Bond length} \propto \frac{1}{\text{Bond order}}$$

Therefore, decreasing order of bond length of these molecular species is: $N_2^{2-} > N_2^{\ominus} = N_2^{\oplus} > N_2$

d. **Comparison of stabilities of $N_2^{\oplus}$ and $N_2^{\ominus}$:** Since both have same bond order, their stabilites should be same. But stability of $N_2^{\oplus}$ > stability of $N_2^{\ominus}$.

This is due to the presence of one e^- in antibonding $(\pi^*\ 2p_x)^1$ MO in $N_2^{\ominus}$

Therefore, decreasing order of stabilities of these molecule species is: $N_2 > N_2^{\oplus} > N_2^{\ominus} > N_2^{2-}$.

The characteristics of the molecular species are summed up in Table 2.18.

15. Oxygen molecule (O_2):

a. $O\ (Z = 8) \Rightarrow 1s^{\,2}\,2s^{\,2}\,2p_x^{\,2}\,2p_y^{\,1}\,2p_z^{\,1}$

Total number of e^-'s in the O_2 molecule $= 8 + 8 = 16$

b. The electronic configuration of O_2 molecule is:

KK* $(\sigma\ 2s)^2\ (\sigma * 2s)^2\ (\sigma\ 2p_z)^2\ (\pi\ 2px^2 \equiv \pi 2p_y^2)$
$(\pi^*\ 2p_x^{\ 1} \equiv \pi\ 2p_y^{\ 1})$

c. **Bond order:**

$N_b = 10\ e^-$'s, $N_a = 6\ e^-$'s $\qquad \text{BO} = \frac{1}{2}(10-6) = 2$

Alternatively: Total number of e^-'s $= 16$

Remaining $p\ e^-$'s $= 16 - 8 = 8$

$N_b = 6$, $N_a = 2$

$\text{BO} = \frac{1}{2}(6-2) = 2$

d. **Nature of bond:** Since BO of O_2 is two, so it contains double bond (O = O).

Table 2.18 Characteristics of N_2, $N_2^{\oplus}$, $N_2^{\ominus}$ and N_2^{2-} ions

Species	Total number of e^-'s	Remaining p e^-'s	BO	Number of unpaired e^-'s	Magnetic character and μ_{MM} value	Stability order
N_2	$7+7=14$	$14-8=6$ $N_b=6$ $N_a=0$	$=\frac{1}{2}(6-0)=3$	0	Diamagnetic and $\mu_{MM}=0$	$N_2 > N_2^{\oplus} > N_2^{\ominus} > N_2^{2-}$
$N_2^{\oplus}$	$7+7-1=13$	$13-8=5$ $N_b=6$ $N_a=0$	$=\frac{1}{2}(5-0)=2.5$	1	Paramagnetic, $\mu_{MM}=\sqrt{3}$ BM	
$N_2^{\ominus}$	$7+7+1=15$	$15-8=7$ $N_b=6$ $N_a=1$	$=\frac{1}{2}(6-1)=2.5$	1	Paramagnetic, $\mu_{MM}=\sqrt{3}$ BM	
N_2^{2-}	$7+7+2=16$	$16-8=8$ $N_b=6$ $N_a=2$	$=\frac{1}{2}(6-2)=2$	2	Paramagnetic, $\mu_{MM}=\sqrt{8}$ BM	

e. **Paramagnetic nature:** O_2 molecule is paramagnetic due to the presence of two unpaired e^-'s in the $\pi^*\,2p_x$ and $\pi^*\,2p_y$ antibonding MO's. Its magnetic moment is:

$$\mu_{MM} = \sqrt{n(n+2)}\ \text{BM}$$
$$= \sqrt{2(2+2)} = \sqrt{8}\ \text{BM}$$

f. Energy level diagram is represented as shown in Fig. 2.85.

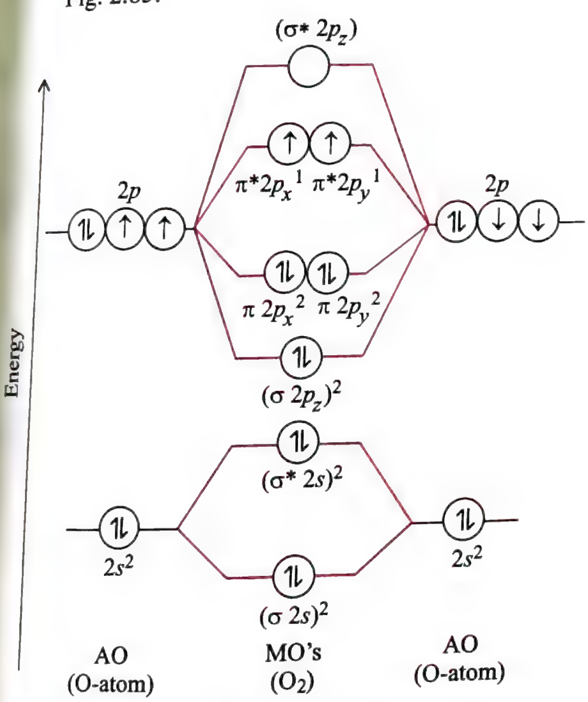


Fig. 2.85 MO energy level diagram for O_2 molecule

g. **No. of σ and π bond in O_2:** $\pi = 1$ and $\sigma = 1$

$2e^-$'s in $\sigma\,(2p_z)^2$ forms 1σ bond

$2e^-$'s in $(\pi\,2p_x)^2$ and 1 e^- in $(\pi^*\,2p_x)^1$ forms 0.5π bond.

$2e^-$'s in $(\pi\,2p_y)^2$ and 1 e^- in $(\pi^*\,2p_y)^1$ forms 0.5π bond.

Total $\pi = 0.5 + 0.5 = 1$

16. $O_2^{\oplus}$, $O_2^{\ominus}$ and O_2^{2-} **ions:**

a. **Dioxygenyl ion ($O_2^{\oplus}$):**

i. It is formed by the loss of one electron from $\pi^*\,2p_x$ or $\pi^*\,2p_y$ MO (refer to Fig. 2.85).

ii. The electronic configuration of $O_2^{\oplus}$ ion is: $KK^*(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x^{\,2} \equiv \pi 2p_y^{\,2})(\pi^* 2p_x^{\,1})$.

iii. **Bond order:**

$N_b = 10, N_a = 5$

$\therefore \text{BO} = \frac{1}{2}(10-5) = 2.5$

Alternatively: Total number of e^-'s $= 16 - 1 = 15$

Remaining p e^-'s $= 15 - 8 = 7$

$N_b = 6, N_a = 1$

$\therefore \text{BO} = \frac{1}{2}(6-1) = 2.5$

iv. **Paramagnetic nature:** $O_2^{\oplus}$ ion is paramagnetic due to the presence of one unpaired e^- in the ($\pi^*\,2p_x$) antibonding MO. Its magnetic moment (μ_{MM}) is $\sqrt{3}$ BM.

v. **No. of σ and π bonds in $O_2^{\oplus}$:** $\pi = 1.5$ and $\sigma = 1$

2 e^-'s in $\sigma\,(2p_z)^2$ forms 1σ bond

$2e^-$'s in $(\pi\,2p_x)^2$ and $1e^-$ in $(\sigma^*\,2p_x)^1$ forms 0.5π bond.

2 e^-'s in $(\pi\,2p_y)^2$ forms 1π bond.

Total $\pi = 0.5 + 1 = 1.5$

b. $O_2^{\ominus}$ **(superoxide ion):**

i. $O_2^{\ominus}$ ion is formed by the gain of one e^- by O_2 molecule. This e^- enters into the $\pi^*\,2p_x$ or $\pi^* 2p_y$ antibonding MO.

ii. The electronic configuration of $O_2^{\ominus}$ ion is: $KK^*\,(\sigma\,2s)^2\,(\sigma\,{}^*2s)^2\,(\sigma\,2p_z)^2\,(\pi\,2p_x^{\,2} \equiv 2p_y^{\,2})\,(\pi^*\,2p_x)^2\,(\pi^*\,2p_y)^1$.

iii. **Bond order:**

$N_b = 10, N_a = 7$

$\therefore \text{BO} = \frac{1}{2}(10-7) = 1.5$

Alternatively: Total number of e^-'s $= 16 + 1 = 17$

Remaining p e^-'s $= 17 - 8 = 9$

$N_b = 6, N_a = 3$

$\therefore$ BO $= \frac{1}{2}(6-3) = 1.5$

iv. **Paramagnetic nature:** It has one unpaired e^- in the π^*2p_y antibonding MO, therefore it is also paramagnetic. Its magnetic moment (μ_{MM}) is $\sqrt{3}$ BM.

v. **No. of σ and π bond in $O_2^{\ominus}$:** $\pi = 0.5$ and $\sigma = 1$

$2e^-$'s in $(\sigma\, 2p_z)^2$ forms 1σ bond

$2e^-$'s in $(\pi\, 2p_x)^2$ and $2\, e^-$'s in $(\pi^*\, 2p_x)^2$ leads to no bond formation and hence zero π bond

$2e^-$'s in $(\pi\, 2p_y)^2$ and $1\, e^-$ in $(\pi^*\, 2p_y)^1$ forms 0.5π bond.

Total $\pi = 0 + 0.5 = 0.5$

c. **O_2^{2-} (Peroxide ion):**

i. O_2^{2-} ion is formed by the gain of two e^-'s by O_2 molecule, these two e^-'s enter into $\pi^*\, 2p_x$ and $\pi^*\, 2p_y$ antibonding MO's, one in each.

ii. The electronic configuration of O_2^{2-} ion is:

KK* $(\sigma\, 2s)^2\, (\sigma^*\, 2s)^2\, (\sigma\, 2p_z)^2\, (\pi\, 2p_x^{\,2} \equiv \pi\, 2p_y^{\,2})\, (\pi^*\, 2p_x^{\,2} \equiv \pi^*\, 2p_y^{\,2})$

iii. **Bond order:**

$N_b = 10\ N_a = 8$

$\therefore$ BO $= \frac{1}{2}(10-8) = 1$

Alternatively: Total number of e^-'s = 16 + 2 = 18

Remaining $p\ e^-$'s = 18 − 8 = 10

$N_b = 6,\quad N_a = 4$

$\therefore$ BO $= \frac{1}{2}(6-4) = 1$

iv. **Diamagnetic nature:** Since it has no unpaired electrons, so it is diamagnetic.

v. **No of σ and π bonds in O_2^{2-}:** $\pi = 0$ and $\sigma = 1$

$2e^-$'s in $(\sigma\, 2p_z)^2$ forms 1σ bond

$2e^-$'s in $(\pi\, 2p_x)^2$ and $2\, e^-$'s in $(\pi^*\, 2p_x)^2$ leads to no bond formation and hence zero π bond

Similarly $2e^-$'s in $(\pi\, 2p_y)^2$ and $2e^-$'s in $(\pi^*\, 2p_y)^2$ leads to no bond formation and hence zero π bond.

Total π = zero.

17. Comparison of characteristics of O_2, $O_2^{\oplus}$, $O_2^{\ominus}$ and O_2^{2-} ions

a. **Bond order:**

$O_2 = 2,\quad O_2^{\oplus} = 2.5$

$O_2^{\ominus} = 1.5,\quad O_2^{2-} = 1$

b. **Bond energy:**

Bond energy ∝ Bond order

∝ Stability

Therefore, decreasing order of bond energies and stabilities molecular species is:

$O_2^{\oplus} > O_2 > O_2^{\ominus} > O_2^{2-}$

c. **Bond length:**

$$\text{Bond length} \propto \frac{1}{\text{Bond order}}$$

Therefore, decreasing order of bond length of these molecular species is:

$O_2^{2-} > O_2^{\ominus} > O_2 > O_2^{\oplus}$

The characteristics of the molecular species are summed up in Table 2.19.

Table 2.19 Characteristics of O_2, $O_2^{\oplus}$, O_2^{2+}, $O_2^{\ominus}$ and O_2^{2-} ions

Species	Total number of e^-'s	Remaining $p\ e^-$'s	Bond order	Number of unpaired e^-'s	Magnetic character and μ_{MM} value	Stability order
O_2 Oxygen	8 + 8 = 16	16 − 8 = 8 $N_b = 6, N_a = 2$	$= \frac{1}{2}(6-2) = 2$	2	Paramagnetic and $\mu_{MM} = \sqrt{8}$ BM	$O_2^{2+} > O_2^{\oplus} > O_2 > O_2^{\ominus} > O_2^{2-}$
$O_2^{\oplus}$ Dioxygenyl ion	8 + 8 − 1 = 15	15 − 8 = 7 $N_b = 6, N_a = 1$	$= \frac{1}{2}(6-1) = 2.5$	1	Paramagnetic and $\mu_{MM} = \sqrt{3}$ BM	
O_2^{2+}	8 + 8 − 2 = 14	14 − 8 = 6 $N_b = 6, N_a = 0$	$= \frac{1}{2}(6-0) = 3.0$	0	Diamagnetic	
$O_2^{\ominus}$ Superoxide ion	8 + 8 + 1 = 17	17 − 8 = 9 $N_b = 6, N_a = 3$	$= \frac{1}{2}(6-3) = 1.5$	1	Paramagnetic $\mu_{MM} = \sqrt{3}$ BM	
O_2^{2-} Peroxide ion	8 + 8 + 2 = 18	18 − 8 = 10 $N_b = 6, N_a = 4$	$= \frac{1}{2}(6-4) = 1$	0	Diamagnetic	

18. **Fluorine molecule (F_2):**

a. F (Z = 9) ⇒ $1s^2\, 2s^2\, 2p_x^2\, 2p_y^2\, 2p_z^1$

Total number of e^-'s in the F_2 molecule = 9 + 9 = 18

b. The electronic configuration of F_2 molecule is:

$KK^*\ (\sigma\ 2s)^2\ (\sigma^*\ 2s)^2\ (\sigma\ 2p_z)^2\ (\pi\ 2p_x^{\ 2} \equiv \pi\ 2p_y^{\ 2})\ (\pi^*\ 2p_x^{\ 2} \equiv \pi^*\ 2p_y^{\ 2})$

c. **Bond order:**

$N_b = 10\ N_a = 8$

$\therefore \text{BO} = \frac{1}{2}(10 - 8) = 1$

Alternatively: Total number of e^-'s = 18

Remaining $p\ e^-$'s = 18 – 8 = 10

$N_b = 6, N_a = 4$

$\therefore \text{BO} = \frac{1}{2}(6 - 4) = 1$

d. **Nature of bond:** Since BO is one, so it contains single bond (F – F).

e. **Diamagnetic nature:** Since it has no unpaired electrons, so it is diamagnetic.

19. **Non-existence of neon molecule (Ne_2):**

a. Ne (Z = 10) ⇒ $1s^2, 2s^2, 2p^6$

Total number of e^-'s in the Ne_2 molecule = 10 + 10 = 20

b. **Bond order:**

$N_b = 10, N_a = 10.$

$\therefore \text{BO} = \frac{1}{2}(10 - 10) = 0$

Zero bond order shows that no bond is formed between 2 – Ne – atoms. Hence, Ne_2 molecule does not exist. Neon exists as monoatomic gas.

2.24.11 Applications of MOT

MOT can be applied to both homonuclear and heteronuclear diatomic molecules as well as to polyatomic molecules.

Summary of the characteristics of some diatomic species having up to 14 e^-'s and more than 14 e^-'s is given in Tables 2.20 and 2.21 respectively.

Table 2.20 Summary of the characteristics of some diatomic species having ≤ 14 e^-'s

Species	Total number of electrons	MO electronic configuration							N_b	N_a	Bond order	Magnetic character
		$\sigma 1s$	$\sigma^* 1s$	$\sigma 2s$	$\sigma^* 2s$	$\pi 2p_x$	$\sigma 2p_y$	$\sigma 2p_z$				
H_2	1 + 1 = 2	2							2	0	1.0	D
$H_2^{\oplus}$	1 + 1 – 1 = 1	1							1	0	0.5	P
He_2	2 + 2 = 4	2	2						2	2	0.0	D
$He_2^{\oplus}$	2 + 2 – 1 = 3	2	1						2	1	0.5	P
Li_2	3 + 3 = 6	2	2	2					4	2	1.0	D
Be_2	4 + 4 = 8	2	2	2	2				4	4	0.0	D
B_2, HF	5 + 5 = 10 and (9 + 1 = 10)	2	2	2	2	1	1		6	4	1.0	P
C_2	6 + 6 = 12	2	2	2	2	2	2		8	4	2.0	D
N_2	7 + 7 = 14	2	2	2	2	2	2	2	10	4	3.0	D
O_2^{2+}	8 + 8 – 2 = 14	2	2	2	2	2	2	2	10	4	3.0	D
$O_2^{\oplus}$	8 + 8 – 1 = 15	2	2	2	2	2	2	1	9	4	2.5	P
$CN^{\ominus}$	6 + 7 + 1 = 14	2	2	2	2	2	2	1	10	4	3.0	D

Note: D = Diamagnetic, P = Paramagnetic.

Table 2.21 Summary of the characteristics of some diatomic species having > 14 e^{-}'s

Species	Total number of electrons	MO electronic configuration										N_b	N_a	Bond order	Magnetic character
		$\sigma 1s$	σ^*1s	$\sigma 2s$	σ^*2s	$\sigma 2p_z$	$\pi 2p_x$	$\pi 2p_y$	$\pi^* 2p_x$	$\pi^* 2p_y$	$\sigma^* 2p_z$				
O_2	16	2	2	2	2	2	2	2	1	1		10	6	2.0	P
$O_2^{\oplus}$	15	2	2	2	2	2	2	2	1			10	5	2.5	P
NO	15	2	2	2	2	2	2	2	1			10	5	2.5	P
$O_2^{\ominus}$	17	2	2	2	2	2	2	2	2	1		10	7	1.5	P
O_2^{2-}	18	2	2	2	2	2	2	2	2	2		10	8	1.0	D
F_2	18	2	2	2	2	2	2	2	2	2		10	8	1.0	D
Ne_2	20	2	2	2	2	2	2	2	2	2	2	10	10	0.0	D

Note: D = Diamagnetic, P = Paramagnetic.

2.24.12 Comparison Between VB and MO Theories

VBT cannot be ruled out completely in the light of MOT. Both the theories have some merits and demerits and none of them is superior to the other. Thus, the study of chemical bonding and molecular behaviour is so complex that even both the theories are still insufficient and imperfect.

1. **Similarities between the two theories:** According to both the theories, we have the following points:
   a. The formation of bond occurs by the overlap of AO's having same energy and same symmetry.
   b. The electron charge lies in the region between the atomic nuclei.
   c. Accounts for directional nature of the bond.
   d. Predicts the non-existence of He_2 and Ne_2.

2. **Difference between the two theories:**

	VBT		MOT
a.	AO's retain their identities. Only valence e^{-}'s take part is bond formation.	a.	AO's lose their identities. All e^{-}'s takes part is bond formation.
b.	Mathematically, it is simple to apply.	b.	It is difficult to apply.
c.	It fails to explain the paramagnetism of O_2.	c.	It explains the paramagnetism of O_2.
d.	It fails to explain the existence of $H_2^{\oplus}$ ion.	d.	It explains the existence of $H_2^{\oplus}$ ion.
e.	Resonance plays an important role.	e.	Resonance has no role.

2.24.13 Examples of Bonding in Some Heteronuclear Diatomic Molecules/Ions

In heteronuclear diatomic molecules/ions, the similar AO's of two atoms do not have equal energies. Hence, their MO energy level diagrams are not symmetrical.

Characteristics of some heteronuclear diatomic molecules/ions are given in Table 2.22.

Table 2.22 Characteristics of some heteronuclear molecules/ions

S. No.	Molecule/ ion	Total number of e^{-}'s	Remaining pe^{-}'s	Electronic configuration of molecules/ ion	Bond order	Number of unpaired e^{-}'s	Magnetic character (μ_{MM} value)
1.	NO	N (Z = 7) O (Z = 8) 7 + 8 = 15	15 − 8 = 7 $N_b = 6$ $N_a = 1$	Order of energy levels and hence filling of MO is same as for homonuclear diatomic molecules with electrons > 14. (i.e. heavier than N_2). Hence, EC of NO = KK* $(\sigma\ 2s)^2 < (\sigma\ ^*2s)^2 < (\sigma\ 2p_z)^2 < (\pi\ 2p_x)^2 \equiv (\pi\ 2p_y)^2 < (\pi^*2p_x)^1$	$\frac{1}{2}(6-1) = 2.5$	1	Paramagnetic $\mu_{MM} = \sqrt{3}$ BM

2.	$NO^{\oplus}$	N (Z = 7) O (Z = 8) 7 + 8 – 1 = 14	14 – 8 = 6 $N_b = 6$ $N_a = 0$	EC of $NO^{\oplus}$ = KK* $(\sigma\ 2s)^2 < (\sigma^*\ 2s)^2 < (\sigma\ 2p_z)^2 \equiv (\pi\ 2p_x)^2 \equiv (\pi\ 2p_y)^2$	$\frac{1}{2}(6-0) = 3$	0	Diamagnetic $\mu_{MM} = 0$
3.	$NO^{\ominus}$	15 + 1 = 16	16 – 8 = 8 $N_b = 6$ $N_a = 2$	The order of filling is same for molecules with e^-'s $\gtrsim$ 14. Hence, EC of $NO^{\ominus}$ = KK* $(\sigma\ 2s)^2 < (\sigma^*\ 2s)^2 < (\sigma\ 2p_z)^2 < (\pi p_x)^2 \equiv (\pi 2p_y)^2 < (\pi^*\ 2p_x)^1 \equiv (\pi^*\ 2p_y)^1$	$\frac{1}{2}(6-2) = 2$	2	Paramagnetic $\mu_{mm} = \sqrt{8}$ BM
4.	BN	B (Z = 5) N (Z = 7) 5 + 7 = 12	12 – 8 = 4 $N_b = 4$ $N_a = 0$	The order of energy levels will be same for molecules with electrons < 14 (i.e. lighter than N_2). Hence, EC of BN = KK* $(\sigma\ 2s)^2 < (\sigma^*\ 2s)^2 < (\pi\ 2p_x)^2 \equiv (\pi\ 2p_y)^2$	$\frac{1}{2}(4-0) = 2$	0	Diamagnetic $\mu_{MM} = 0$
5.	$CN^{\ominus}$	C (Z = 6) N (Z = 7) 6 + 7 + 1 = 14	14 – 8 = 16 $N_b = 6$ $N_a = 0$	The order of filling of MO's should be same as for N_2. Hence, EC of $CN^{\ominus}$ = KK* $(\sigma\ 2s)^2 < (\sigma\ {}^*2s)^2 < (\pi\ 2p_x)^2 \equiv (\pi\ 2p_y)^2 < (\sigma\ 2p_z)^2$	$\frac{1}{2}(6-0) = 3$	0	Diamagnetic $\mu_{MM} = 0$
6.	CN	C (Z = 6) N (Z = 7) 6 + 7 = 13	13 – 8 = 5 $N_b = 5$ $N_a = 0$	The order of filling of MO's will be same for molecules with electrons < 14. Hence, EC of CN = KK* $(\sigma\ 2s)^2 < (\sigma\ {}^*\ 2s)^2 < (\pi\ 2p_x)^2 \equiv (\pi\ 2p_y)^2 < (\sigma\ 2p_z)^1$	$\frac{1}{2}(5-0) = 2.5$	1	Paramagnetic $\mu_{MM} = \sqrt{3}$ BM
7.	$CN^{\oplus}$	C (Z = 6) N (Z = 7) 6 + 7 – 1 = 12	12 – 8 = 4 $N_b = 4$ $N_a = 0$	The order of filling of MO's will be same for molecule with electrons < 14. Hence, EC of $CN^{\oplus}$ = KK* $(\sigma\ 2s)^2 < (\sigma\ {}^*\ 2s)^2 < (\pi\ 2p_x)^2 \equiv (\pi\ 2p_y)^2$	$\frac{1}{2}(4-0) = 2$	0	Diamagnetic $\mu_{MM} = 0.$
8.	CO	C (Z = 6) O (Z = 8) 6 + 8 = 14	14 – 8 = 6 $N_b = 6$ $N_a = 0$	Number of electrons = 14. Thus order of filling of MO should be same as for N_2. Expected EC of CO : KK* $(\sigma\ 2s)^2 < (\sigma\ {}^*\ 2s)^2 < (\pi\ 2p_x)^2 \equiv (\pi\ 2p_y)^2 < (\sigma\ 2p_z)^2$	Expected bond order $= \frac{1}{2}(6-0) = 3$	0	Diamagnetic $\mu_{MM} = 0.$
9.	$CO^{\oplus}$	14 – 1 = 13	13 – 8 = 5 $N_b = 5$ $N_a = 0$	Expected EC of $CO^{\oplus}$: KK* $(\sigma\ 2s)^2 < (\sigma\ {}^*\ 2s)^2 < (\pi\ 2p_x)^2 \equiv (\pi\ 2p_y)^2 < (\sigma\ 2p_z)^1$	Expected bond order $= \frac{1}{2}(5-0) = 2.5$	1	Paramagnetic $\mu_{MM} = \sqrt{3}$ BM

Note: Exception in the EC of CO and $CO^{\oplus}$ molecule/ ion: It was observed that BO of $CO^{\oplus}$ > BO of CO contrary to expected BO. This is possible only if electron were removed from antibonding MO. It was also found that 2s orbital of O-atom has lower energy than 2s orbital of C–atom. When they mix to form $(\sigma\ 2s)$ and $(\sigma\ {}^*2s)$ orbitals, the latter has so high energy that it goes above $(\sigma\ 2p_z)$ as well as $(\pi\ 2p_x)$ and $(\pi\ 2p_y)$ orbitals. Thus correct ECof CO_2 is : KK* $(\sigma\ 2s)^2 < (\pi\ 2p_x)^2 \equiv (\pi\ 2p_y)^2 < (\sigma\ 2p_z)^2 < (\sigma\ {}^*\ 2s)^2$ and that of $CO^{\oplus}$ is: KK* $(\sigma\ 2s)^2 < (\pi\ 2p_x)^2 \equiv (\pi\ 2p_y)^2 < (\sigma\ 2p_z)^2 < (\sigma\ {}^*\ 2s)^1$

$$\therefore \text{BO of CO} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10-4) = 3$$

$$\text{BO of } CO^{\oplus} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10-3) = 3.5$$

In fact, bond length of CO = 1.128 Å and of $CO^{\oplus}$ = 1.115 Å. Thus bond length decreases when we expected it to increase. Therefore, the order of MO energy levels for simple homonuclear diatomic molecule is not necessary. The same is applicable for heteronuclear diatomic molecule.

2.25 GERADE (g) AND UNGERADE (u) MO's

If the symmetry of a MO with respect to its centre is symmetrical, it is called gerade (gerade in German means symmetrical) and it is represented by symbol 'g'. If it unsymmetrical, it is called ungerade and is represented by symbol 'u'.

The symmetry in the orbitals is a point from which lines when drawn on one side and produced to an equal distance on the other side will meet the new point. If at this new point, the sign for the orbital is same, it is gerade, otherwise ungerade.

All 'σ' (bonding MO's) are gerade whereas all 'σ*' (antibonding MO's) are ungerade. Similarly, all 'π*' (antibonding MO's) are gerade whereas all 'π' (bonding MO's) are ungerade, for example,

Gerade orbitals: $\sigma_g(1s)$, $\sigma_g(2s)$, $\sigma_g(2p_z)$, $\pi^*_g(2p_x)$, $\pi^*_g(2p_y)$

Ungerade orbitals: $\sigma^*_u(1s)$, $\sigma^*_u(2s)$, $\sigma^*_u(2p_z)$, $\pi_u(2p_x)$, $\pi_u(2p_y)$

These are shown in Fig. 2.86.

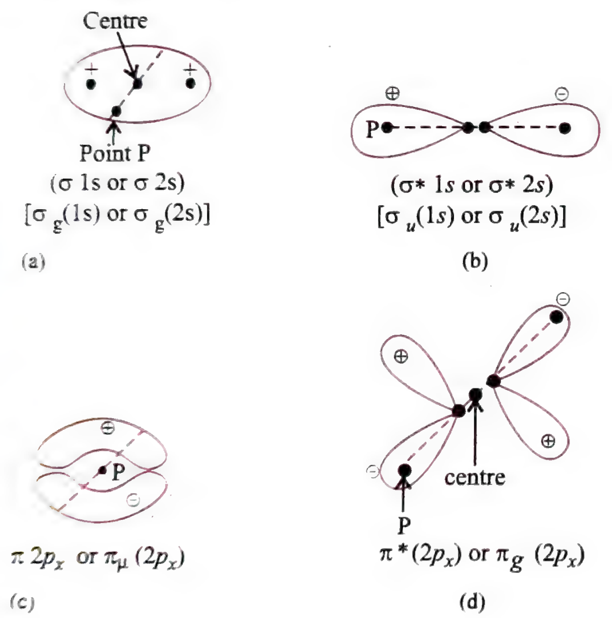
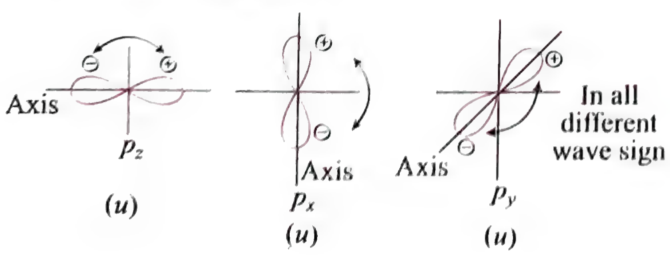


Fig. 2.86 Representation of gerade and ungerade MO's

2.25.1 GERADE AND UNGERADE s, p AND d ORBITALS

1. All s orbitals are gerade (g).
2. All p orbitals are ungerade (u).



3. All d-orbitals are gerade.

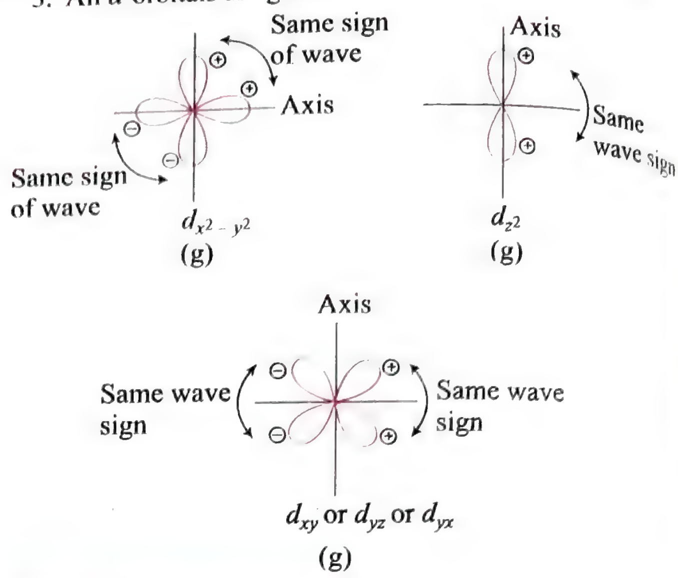


ILLUSTRATION 2.33

Consider the following orbitals:

(I) $4p_x$ (II) $3d_{z^2}$ (III) $4d_{x^2-y^2}$ (IV) $4d_{xy}$

Then, calculate the value of "$a + b + c$".

a = Total number of gerade orbitals in the above given orbitals

b = Total number of ungerade orbitals in the above given orbitals

c = Total number of axial orbitals in the above given orbitals

Sol. (7)

(i) All p orbitals are ungerade (u).

(ii) All d orbitals are gerade (g).

(I) $g = 0, u = 1$, (II) $g = 1, u = 0$ (III) $g = 1, u = 0$

(IV) $g = 1, u = 0$.

Total 'g' = 0 + 1 + 1 + 1 = 3 = a.

Total 'u' = 1 + 0 + 0 + 0 = 1 = b.

(iii) All p orbitals are axial orbitals.

(iv) d_{z^2} and $d_{x^2-y^2}$ are axial orbitals.

No. of axial orbitals

(I) $4p_x = 1$, (II) $3d_{z^2} = 1$, (III) $4d_{x^2-y^2} = 1$, (IV) $4d_{xy} = 0$

Total 'c' = 1 + 1 + 1 + 0 = 3.

$\therefore a + b + c = 3 + 1 + 3 = 7$.

ILLUSTRATION 2.34

Compare the bond length of O–O in the following molecules

a. KO_2 **b.** $O_2\ [AsF_6]$

c. O_2 **d.** Na_2O_2

Sol.

a. KO_2 has $O_2^{\ominus}$ (superoxide ion), Bond order = 1.5

b. $O_2\ [AsF_6]$ has $O_2^{\oplus}$, Bond order = 2.5

c. O_2, Bond order = 2

d. Na_2O_2 has O_2^{2-} (peroxide ion), Bond order = 1

Higher is the BO, smaller is the bond length. Hence, order of bond length is:

$O_2^{\oplus} < O_2 < O_2^{\ominus} < O_2^{2-}$

ILLUSTRATION 2.35

Which diatomic molecule of second period besides O_2 should be paramagnetic?

Sol. B_2: $(\sigma\ 1s)^2\ (\sigma\ {*1s})^2\ (\sigma\ 2s)^2\ (\sigma\ {*2s})^2\ (\pi\ 2p_x)^1 = (\pi\ 2p_y)^1$

As paramagnetism arises due to unpaired electron. Therefore, B_2 is a paramagnetic molecule.

ILLUSTRATION 2.36

a. Write the molecular orbital electron distribution of oxygen (O_2). Specify its bond order and magnetic property.

b. Fill in the blanks:

When N_2 goes to $N_2^{\oplus}$, the N–N bond distance ______ and when O_2 goes to $O_2^{\oplus}$, the O–O bond distance ______.

Sol.

a. O_2: KK* $(\sigma\ 2s)^2\ (\sigma\ {*2s})^2\ (\sigma\ 2p_z)^2\ (\pi\ 2p_x)^2\ (\pi\ 2p_y)^2\ (\pi\ {*2p_x})^1\ (\pi\ {*2p_y})^1$

$$\text{Bond order} = \frac{1}{2}(8-4)$$
$$= 2$$

The molecule is paramagnetic due to two unpaired electrons in $(\pi\ {*2p_x})^1\ (\pi\ {*2p_y})^1$.

b. Increases, decreases.

ILLUSTRATION 2.37

Which of the two, peroxide ion or superoxide ion, has larger bond length?

Sol. The bond length in a molecule is dependent on bond order. The higher is the bond order, smaller will be the bond length.

Peroxide ion, O_2^{2-}

O_2^{2-}: KK* $(\sigma\ 2s)^2\ (\sigma\ {*2s})^2\ (\sigma\ 2p_z)^2\ (\pi\ 2p_x)^2\ (\pi\ 2p_y)^2\ (\pi\ {*2p_x})^2\ (\sigma\ {*2p_y})^2$

$$\text{Bond order} = \frac{10-8}{2} = 1$$

Superoxide ion, $O_2^{\ominus}$

$O_2^{\ominus}$: KK* $(\sigma\ 2s)^2\ (\sigma\ {*2s})^2\ (\sigma\ 2p_z)^2\ (\pi\ 2p_x)^2\ (\pi\ 2p_y)^2\ (\pi\ {*2p_x})^2\ (\pi\ {*2p_y})^1$

$$\text{Bond order} = \frac{10-7}{2} = 1.5$$

Bond order of superoxide ion is higher than peorxide ion, hence bond length of peroxide ion is larger.

ILLUSTRATION 2.38

a. How the bond energy varies from $N_2^{\ominus}$ and $N_2^{\oplus}$ and why?

b. On the basis of molecular orbital theory what is the similarity between

i. F_2 and O_2^{2-} ii. CO, N_2 and $NO^{\oplus}$?

Sol.

a. Bond energy of $N_2^{\oplus}$ = Bond energy of $N_2^{\ominus}$ because the bond order is same in both the species. [However, $N_2^{\oplus}$ is slightly more stable than $N_2^{\ominus}$ as number of antibonding electrons is higher in $N_2^{\ominus}$ than $N_2^{\oplus}$.]

b. i. Both F_2 and O_2^{2-} have same bond order, same bond length and are diamagnetic.

ii. These are isoelectronic species, possess same bond order and same bond length.

ILLUSTRATION 2.39

Select from the following molecular orbitals which are gerade and ungerade.

a. $\sigma\ (2s)$ b. $\pi\ {*}(2p_x)$ c. $\pi\ {*}(2p_y)$

d. $\sigma\ {*}(1s)$, e. $\pi\ (2p_x)$ f. $\pi\ (2p_y)$

Sol. All σ bonding MO's and all π antibonding MO's (i.e. π *) are gerade.

Whereas all σ antibonding MO's (i.e. σ *) and all π bonding MO's are ungerade.

Gerade molecular orbitals (represented by 'g') are:

a. $\sigma\ g\ (2s)$ b. $\pi\ {*}_g\ 2p_x$ c. $\pi\ {*}_g\ 2p_y$

Ungerade MO's (represented by 'u') are:

d. $\sigma\ {*}_u\ (1s)$ e. $\pi_u\ (2p_x)$ f. $\pi_u\ (2p_y)$

CONCEPT APPLICATION EXERCISE 2.2

1. Arrange the following types of interaction in order of decreasing stability:
   a. Covalent bond b. van der Waals force
   c. H-bonding d. Dipole interaction
   e. Ionic bond
2. Arrange the following types of intermolecular forces in order of decreasing their strength.
   a. Ion dipole b. Keesom forces
   c. Dispersion or London forces
   d. Dipole-induced dipole
   e. Ion-induced dipole (Debye forces)
3. Name the types of interaction or intermolecular forces of which potential energy–distance function are given below:

   a. $E \propto \frac{1}{r}$ b. $E \propto \frac{1}{r^2}$ c. $E \propto \frac{1}{r^3}$

   d. $E \propto \frac{1}{r^4}$ e. $E \propto \frac{1}{r^6}$

4. a. List properties of water that stem from H-bonding.

   b. The two molecules indicated below are capable of forming interamolecular H-bonding. Which is likely to form more stable H-bonds. Give reasons.

   i. $CH_3\,COCH=\overset{\overset{\displaystyle CH_3}{|}}{C}-OH$

   ii. $CH_3\,COCH_2\,\overset{\overset{\displaystyle CH_3}{|}}{CH}-OH$

5. a. Predict the order of decreasing boiling points of noble gases.

   b. Predict the order of decreasing boiling points of the followings: H_2, He, Ne, Xe, CH_4.

6. Which one of the following pairs is expected to exhibit H-bonding.

   a. CH_3CH_2OH and CH_3OCH_3

   b. CH_3NH_2 and CH_3SH

   c. CH_3OH and $(CH_3)_3N$

7. a. Give the decreasing order of melting points of the following: NH_3, PH_3, $(CH_3)_3N$. Explain.

   b. In which molecule is the van der Waals force likely to be the most important in determining the m.pt. and b.pt. for ICl, Br_2, HCl, H_2S, CO.

8. a. How many nodal planes are present in the following MO's. (Taking Z-axis as the internuclear axis)

   i. $\sigma\,1s$ ii. $\sigma\,{*1s}$ iii. $\sigma\,2p_z$ iv. $\sigma\,{*2p_z}$

   v. $\pi\,2p_x$ or $\pi\,2p_y$ vi. $\pi{*2p_x}$ or $\pi{*2p_y}$

   b. Give the number of electrons which occupy the bonding orbitals in $H_2^{\oplus}$, H_2 and $O_2^{\oplus}$.

   c. Why N_2 has greater bond dissociation energy than $N_2^{\oplus}$ whereas $O_2^{\oplus}$ has greater bond dissociation energy than O_2.

9. Compare the relative stabilities and magnetic behaviour of the following species.

   a. $O_2^{\ominus}$ and $N_2^{\oplus}$ b. O_2^{2-} and $N_2^{\ominus}$

   c. O_2^{2-} and N_2^{2-}

10. Explain:

    a. $H_2^{\oplus}$ and $H_2^{\ominus}$ ions have same bond order but $H_2^{\oplus}$ ions are more stable than $H_2^{\ominus}$.

    b. It is possible to have a diatomic molecule with its ground state MO's full with electrons.

    c. Why $2p_x$ or $2p_y$ orbitals do not combine with $2s$ orbitals to form MO. (Taking Z-axis as the internuclear axis)

11. Which of the following species have same bond order and same shape?

    a. $N_3^{\ominus}$ b. O_3 c. CO_2 d. $NO_2^{\ominus}$

Solved Examples

Ionic and Covalent Bonding

EXAMPLE 2.1

Construct a table comparing metals with non-metals in terms of

a. The sign of the charges possible on monoatomic ions.

b. The possibility of reaction with other elements of the same class.

c. The range of the possible number of valence electrons.

d. The ability of the elements to conduct electricity in the elementary state.

Sol.

	a.	b.	c.	d.
Metals	+	unusual	1–5	all
Non-metals	–	normal	3–8	few

EXAMPLE 2.2

a. In which of the following compounds is the bonding essentially ionic, in which is the bonding essentially covalent and in which are both types of bonding represented?

   i. C_2H_5OH ii. NaBr

   iii. $Ba(CN)_2$ iv. $(NH_4)_2S$

   v. PCl_3

b. Write the formula for a compound of Cl which contains (i) Ionic bonds only, (ii) Ionic and covalent bonds and (iii) Covalent bonds only.

c. Covalent bonds are called directional while ionic bonds are called non-directional. Explain.

Sol.

a. i. Covalent ii. Ionic iii. Both

   iv. Both v. Covalent

Note: $NH_4^{\oplus}$ (ammonium ion) and $CN^{\ominus}$ (cyanide ion) have covalently bonded atoms within the ions.

b. One possible for each.

   i. NaCl ii. NaClO iii. NCl_3

c. Covalent bonds are directional because it is formed by the overlap of hybridised orbitals which is also directional.

EXAMPLE 2.3

Pure liquid H_2SO_4 solidifies below 10.4°C. Neither the pure liquid nor the solid conducts electricity; however, aqueous solution of H_2SO_4 conducts electricity.

Solid Na_2SO_4, which melts at 884°C, does not conduct electricity, but molten Na_2SO_4 as well as aqueous solutions of Na_2SO_4 conduct electricity. Explain the difference in properties between pure Na_2SO_4 and H_2SO_4.

H_2SO_4	Na_2SO_4
Pure H_2SO_4 is essentially covalent.	It is ionic with $Na^{\oplus}$ and SO_4^{2-} ions.
It does not conduct electricity because there are no ions to carry the charge.	It does not conduct because ions are not free to move.
When H_2SO_4 dissolves, it reacts with H_2O to form ions and the solution conducts well.	When Na_2SO_4 is melted or dissolved, the ions are freed and conducted well.

Electron Dot Structure and the Octet Rule

EXAMPLE 2.4

Write electron dot and line structure for:

a. SeO_3^{2-} b. Li_3PO_4 c. $ClO_2^{\ominus}$ d. $COCl_2$

e. H_2CO f. C_2H_2 g. HCO_2H

Refer to Illustration 2.4 (Second method).

Note: Electrons in circle O represent unshared e⁻'s.
Electrons in rectangle □ represent shared e⁻'s.

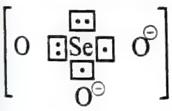
a. SeO_3^{2-}:

i. V (Total number of valence e^-'s) = $6 + 3 \times 6 + 2 = 26\ e^-$'s

ii. O (Total number of e^-'s for octet) = $8 + 3 \times 8 = 32\ e^-$'s

iii. S (Shared e^-'s) = (O – V) = (32 – 26) = 6 e^-'s

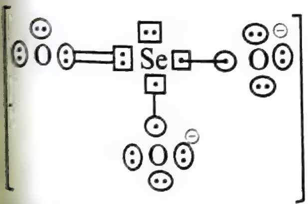
iv. Skeletal structure with 6 shared e^-'s



(6 shared e^-'s)

v. U (unshared e^-'s) = (V – S) = (26 – 6) = 20 e^-'s

vi. Add 20 unshared e^-'s to complete the Lewis dot structure.



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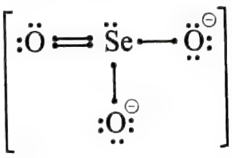


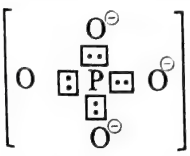
b. PO_4^{3-}:

i. $V = 5 + 4 \times 6 + 3 = 32\ e^-$'s

ii. $O = 8 + 4 \times 8 = 40\ e^-$'s

iii. $S = (O - V) = (40 - 32) = 8\ e^-$'s

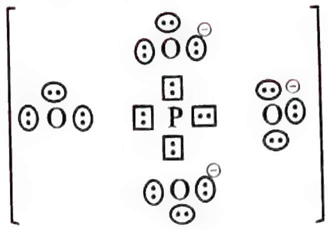
iv. Skeletal structure with 8 shared e^-'s.



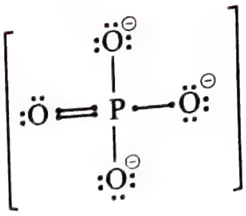
(8 shares e^-'s)

v. $U = (V - S) = (32 - 8) = 24\ e^-$'s

vi. Add 24 e^-'s to complete the Lewis dot structure.



or



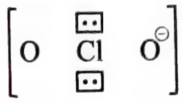
c. $ClO_2^{\ominus}$:

i. $V = 7 + 2 \times 6 + 1 = 20\ e^-$'s

ii. $O = 8 + 2 \times 8 = 24\ e^-$'s

iii. $S = (O - V) = (24 - 20) = 4\ e^-$'s

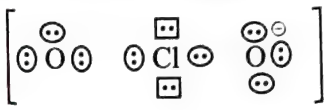
iv. Skeletal structure with 4 shared e^-'s.



(4 shared e^-'s)

v. $U = (V - S) = (20 - 4) = 16\ e^-$'s

vi. Add 16 e^-'s to complete the Lewis dot structure.



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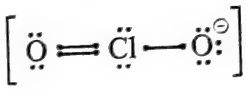


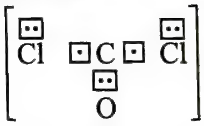
d. $COCl_2$:

i. $V = 4 + 6 + 2 \times 7 = 24\ e^-$'s

ii. $O = 8 + 8 + 2 \times 8 = 32\ e^-$'s

iii. $S = (O - V) = (32 - 24) = 8\ e^-$'s

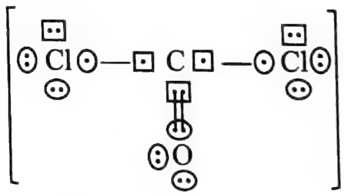
iv. Skeletal structure with 8 shared e^-'s



(8 shared e^-'s)

v. $U = (V - S) = (24 - 8) = 16\ e^-$'s

vi. Add 16 e^-'s to complete the Lewis dot structure.



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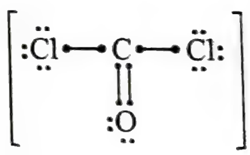


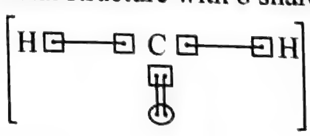
e. H_2CO:

i. $V = 1 \times 2 + 4 + 6 = 12\ e^-$'s

ii. $O = 2 \times 2 + 8 + 8 = 20\ e^-$'s

iii. $S = (O - V) = (20 - 12) = 8\ e^-$'s

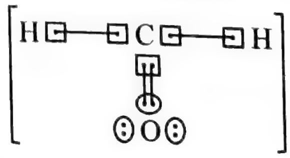
iv. Skeletal structure with 8 shared e^-'s



(8 shared e^-'s)

v. $U = (V - S) = (12 - 8) = 4\ e^-$'s

vi. Add 4 e^-'s to complete the Lewis dot structure.



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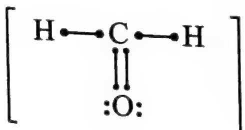


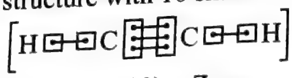
f. C_2H_2:

i. $V = 2 \times 4 + 1 \times 2 = 10\ e^-$'s

ii. $O = 2 \times 8 + 2 \times 2 = 20\ e^-$'s

iii. $S = (O - V) = (20 - 10) = 10\ e^-$'s

iv. Skeletal structure with 10 shared e^-'s



v. $U = (V - S) = (10 - 10) =$ Zero

vi. Hence skeletal structure is the Lewis dot structure.

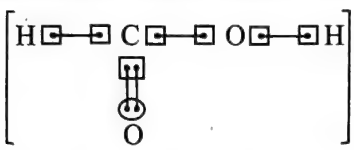
g. HCO_2H :

i. $V = 1 + 4 + 2 \times 6 + 1 = 18\ e^-$'s

ii. $O = 2 + 8 + 2 \times 8 + 2 = 28\ e^-$'s

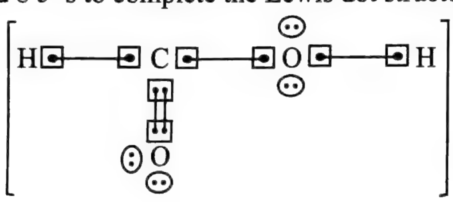
iii. $S = (O - V) = (28 - 18) = 10\ e^-$'s

iv. Skeletal structure with 10 shared e^-'s



v. $U = (V - S) = (18 - 10) = 8\ e^-$'s

vi. Add 8 e^-'s to complete the Lewis dot structure.



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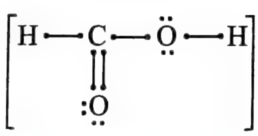


Formal Charges

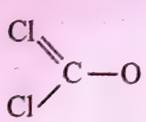
EXAMPLE 2.5

By completing the following structures, adding unshared e^- pairs when necessary, calculate the formal charges.

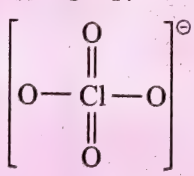
a. $N \equiv C - C \equiv N$

b. $Cl - C \equiv N$

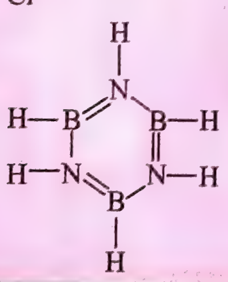
c.



d.



e.



Sol. FC on an atom = [Total no. of valence e^-'s (V)] − [Total no. of non-bonding e^-'s (nb)] $-\frac{1}{2}$ [Total no. of bonding e^-'s (b)]

(or) $FC = (V) - (nb) - \frac{1}{2}(b)$

a. $\ddot{N} \equiv C — C \equiv \ddot{N}$ (All zero)

$FC \text{ on } N = (V) - (nb) - \frac{1}{2}(b) = 5 - 2 - \frac{1}{2} \times 6 =$ Zero

$FC \text{ on } C = 4 - 0 - \frac{1}{2} \times 8 =$ Zero

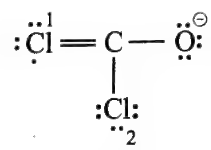
b. $[:\ddot{Cl} — C \equiv \ddot{N}]$ (All zero)

$FC \text{ on } Cl = (V) - (nb) - \frac{1}{2}(b) = 7 - 6 - \frac{1}{2} \times 2 =$ Zero

$FC \text{ on } C = 4 - 0 - \frac{1}{2} \times 8 =$ Zero

$FC \text{ on } N = 5 - 2 - \frac{1}{2} \times 6 =$ Zero

c.



[+1 on doubly bonded Cl, −1 on O, zero on another Cl]

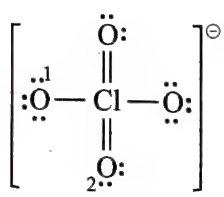
$FC \text{ on } Cl^1 = 7 - 4 - \frac{1}{2} \times 4 = +1$

$FC \text{ on } Cl^2 = 7 - 6 - \frac{1}{2} \times 2 =$ Zero

$FC \text{ on } C = 4 - 0 - \frac{1}{2} \times 8 =$ Zero

$FC \text{ on } O = 6 - 6 - \frac{1}{2} \times 2 = -1$

d.



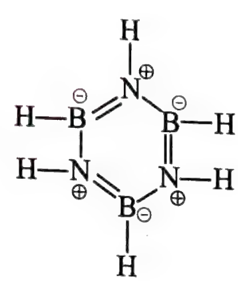
[+1 on Cl, −1 on each singly bonded O-atom and zero on each doubly bonded O-atom.

$FC \text{ on } Cl = 7 - 0 - \frac{1}{2} \times 12 = +1$

$FC \text{ on } O^1 = 6 - 6 - \frac{1}{2} \times 2 = -1$

$FC \text{ on } O^2 = 6 - 4 - \frac{1}{2} \times 4 =$ Zero

e.



[+1 on each N, −1 on each B-atom]

$$\text{FC on N} = 5 - 0 - \frac{1}{2} \times 8 = +1$$

$$\text{FC on B} = 3 - 0 - \frac{1}{2} \times 8 = -1$$

Resonance

EXAMPLE 2.6

a. In each of the following paris, select the species having the greater resonance stabilisation.

i. $H_2O = O$ and $HC(=O)-O^{\ominus}$

ii. HNO_3 and $NO_3^{\ominus}$

b. Draw all possible octet structural formulas for $N_3^{\ominus}$. Which ones are possible resonance forms?

Sol.

a.

i. $HC(=O)-O^{\ominus}$ has two equal resonance forms, as shown:

$$HC(=O)-O^{\ominus} \leftrightarrow HC(-O^{\ominus})=O$$

$H_2C = O$ does not have other resonance forms as low in energy.

Note: $H_2C^{\oplus}-\ddot{O}:^{\ominus}$ contributes some but $H_2C - O^{\oplus}$ contributes little.

ii. $NO_3^{\ominus}$ has three equal energy resonance forms; HNO_3 has only two, since the O-atom bonded to the H-atom is not equivalent to the others.

b. The possible linear structures are shown as:

$$\left[:\ddot{N}=N=\ddot{N}:\right]^{\ominus} \leftrightarrow \left[:\ddot{\underset{\cdot\cdot}{N}}-N\equiv N:\right]^{\ominus} \leftrightarrow \left[N\equiv N-\ddot{\underset{\cdot\cdot}{N}}:\right]^{\ominus}$$

I II III

$$\left[\begin{array}{c} :N=N: \\ \backslash\ / \\ :N: \end{array}\right]^{\ominus}$$

IV

In two resonance structures (II) and (III) one of the terminal N-atom in an isolated $N_3^{\ominus}$ ion should be different from the other.

The structure (IV) although satisfies octet rule is ruled out as a resonance form because the atoms are in different positions. Moreover, the structure (IV) has considerable strain.

Dipole Moment

EXAMPLE 2.7

Answer the following:

a. Distinguish between a polar bond and a polar molecule. To which does the term dipole refer ?

b. Which is having the higher b.pt.: Br_2 or ICl.

c. i. Can a molecule have a dipole moment if it has no polar covalent bonds?

ii. How is it possible for a molecule to have polar bonds but no dipole moment?

d. Arrange in decreasing polarity of bonds: SbH_3, AsH_3, PH_3, NH_3.

Sol.

a. A polar bond is formed between two atoms of different EN. A polar molecule results when there is only one polar bond or when more than one polar bond within it is not sufficiently oriented to cancel the effects of the others.

The polar molecule is often referred to as having a dipole moment.

b. Both of these molecules have same number of electrons but ICl has a dipole moment, So, ICl have higher b.pt.

c. i. No.

ii. If the various polar bonds are arranged symmetrically, as in CO_2 and CCl_4, the effects of one bond are cancelled by the effects of the other(s).

d. Greater the difference in EN of the atoms, more polarity of bonds.

	EN	Difference in EN in	Decreasing order of polarity of bonds
H	2.1	$PH_3 = 2.1 - 2.1 = 0$	
Sb	1.9	$AsH_3 = 2.1 - 2.0 = 0.1$	$NH_3 > SbH_3 > AsH_3 > PH_3$
As	2.0	$SbH_3 = 2.1 - 1.9 = 0.2$	
P	2.1		
N	3.0	$NH_3 = 3.0 - 2.1 = 0.9$	

EXAMPLE 2.8

a. The decreasing order of dipole moment of $SO_2 > NH_3 > AsH_3 > BF_3 > CO_2$ ($\mu = 0$). What can be concluded about the shapes of the molecules?

b. What is the value of 1D in S1 units.

c. The dipole moment of HBr is 2.60×10^{-30} Cm, and the interatomic spacing is 1.41 Å. What is the percentage of ionic character of HBr ?

Sol.

a.

i. $SO_2 \Rightarrow$ Bent   ii. $NH_3 \Rightarrow$ Pyramidal

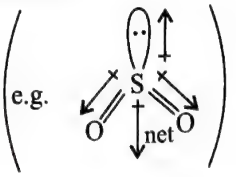
iii. $AsH_3 \Rightarrow$ Pyramidal   iv. $BF_3 \Rightarrow$ Planar

v. $CO_2 \Rightarrow$ Linear ($\mu = 0$)

E N of O > S or C. Each S – O and C – O bond should be polar, with a –ve charge on the O-atom.

Since CO_2 has no net dipole moment, the two C – O bond moment must exactly cancel. This can occur only if the two bonds are in a straight line, i.e. linear (e.g.: $O=C=O$ $\mu_{net} = 0$).

The existence of dipole moment in SO_2 suggests that molecule is bent.



NH_3 and AsH_3 are both pyramidal but BF_3 is planar. From the dipole moments alone, nothing can be concluded about the relative flatness of the NH_3 and AsH_3 pyramids, because the EN's of N and As are different.

b. $ID = (10^{-18}\text{ esu cm})$ and $1C = 2.998\times10^{9}$ esu.

$$ID = (10^{-18}\text{ esu cm})\left(\frac{1C}{2.998\times10^{9}\text{ esu}}\right)\left(\frac{1\text{ m}}{10^{2}\text{ cm}}\right) = 3.336$$

$\times\ 10^{-30}$ Cm

c. $$\%\text{ ionic character} = \frac{\mu_{obs}}{\mu_{cal}}$$

$$= \frac{2.60\times10^{-30}\text{Cm}}{(1.60\times10^{-19}\text{ C})\ (1.41\times10^{-10}\text{ m})}$$

$$= \frac{2.60\times10^{-30}\text{Cm}}{2.26\times10^{-29}\text{ Cm}} = 11.5\%$$

Bond Lengths and Bond Energies

EXAMPLE 2.9

The single and multiple bond radii of some elements are given in the following tables.

Single bond radii (Å)					
H	0.28	P	1.10	Te	1.37
C	0.77	As	1.21	F	0.64
Si	1.77	Sb	1.41	Cl	0.99
Ge	1.22	O	0.66	Br	1.14
Sn	1.40	S	1.04	I	1.33
N	0.70	Se	1.17		

Multiple bond radii (Å)	
C =	0.67
C ≡	0.61
N =	0.63
N ≡	0.55

Calculate the bond lengths in:

a. SCl_2 **b.** NH_3 **c.** CH_2Cl_2 **d.** HOCl
e. HCN **f.** H_3PO_4 **g.** CH_3NH_2

Sol. Covalent bond radii from the given table are merely added.

a. $(1.04 + 0.99) = 2.03$ Å

b. $(0.70 + 0.28) = 0.98$ Å

c. $C - H = (0.77 + 0.28) = 1.05$ Å

$C - Cl = (0.77 + 0.99) = 1.76$ Å

d. $H - O = 0.94$ Å

$O - Cl = 1.65$ Å

e. $H - C = 1.05$ Å

$(C \equiv N) = (0.61 + 0.55) = 1.16$ Å

f. $H - O = 0.94$ Å

$O - P = 1.76$ Å

g. $C - H = 1.05$ Å

$C - N = 1.74$ Å $\quad N - H = 0.98$ Å

EXAMPLE 2.10

a. Arrange $C - C$, $C = C$ and $C \equiv C$ in order of:

i. Decreasing bond energy

ii. Decreasing bond lengths

b. The As–Cl bond distance in $AsCl_3$ is 2.20 Å. Estimate the single-bond covalent radius of As.

Sol.

a. i. $C \equiv C > C = C > C - C$

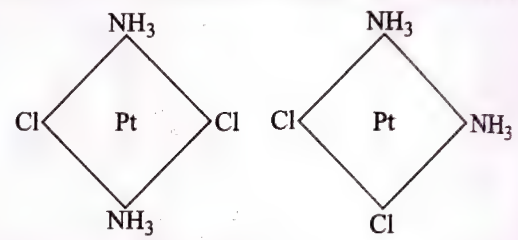
ii. $C - C > C = C > C \equiv C$

b. Internuclear distance – Radius of chlorine atom = Radius of As atom

$\therefore\ (2.20 - 0.99) = 1.21$ Å

EXAMPLE 2.11

The Pt–Cl distance is 2.32 Å in several crystaline compounds. What is the Cl–Cl distance in structures (i) and in (ii)?



(i) (ii)

Sol. In structure (i):

$Cl - Cl = 2\ (2.32) = 4.64$ Å

In structure (ii):

Using the pythagorean theorem, we have

$Cl - Cl = \sqrt{2}\ (2.32) = 3.28$ Å.

EXAMPLE 2.12

a. The average $(C - C)$ bond energy is 343 kJ mol^{-1}. What do you predict for the Si–Si single bond energy?

b. Carborundum (SiC) and corundum (Al_2O_3) are important abrasives. Comment on the structures for these compounds to explain why they have such hardness.

Sol.

a. Covalent bonds between the 3rd Period non-metals are generally weaker than the bonds between atoms of their 2nd period neighbours. Si–Si bonds are expected to be weaker than C–C bonds. Their bond strength should be less than 300 kJ mol^{-1}.

b. The hardness results from the fact that the atoms are bonded together in three-dimensional arrays by strong bonds. SiC has the diamond structure. The bonds in Al_2O_3 have ionic character as well as covalent.

EXAMPLE 2.13

Answer the following:

a. Compare the shapes of p-orbital and an sp-hybrid orbital. Which one has a greater directional orientation?

b. What are the hybridisation state of each C-atom in the following molecules ?

i. Benzene   ii. $CH_3\,CH_2\,CH_2\,CH_3$

iii. $HC \equiv CH$ iv. $CH_2 = CH - CH = CH_2$

v. $CH_3 - CH = CH - CH_3$

c. What hybridisation is expected on the central atom of each of the following molecules?

i. BF_3 ii. $PF_6^{\ominus}$ iii. CH_2Cl_2 iv. BeH_2

d. i. Which molecule, AX_3, AX_4, AX_5, AX_6 is likely to have a trigonal bipyramid structure.

ii. If the central atom A, has no lone pairs, what type of hybridisation will it have.

Sol.

a. The p-orbital has equal sized lobes; most of the sp probability density is on one side, making the latter more directional in character.

b. i. All sp^2 ii. All sp^3 iii. Both sp

iv. All sp^2 v. sp^3, sp^2, sp^2, sp^3

c. i. sp^2 ii. sp^3d^2 iii. sp^3

iv. sp

d. i. AX_5 is the only molecule with five atoms bonded to central atom, it is only possible molecule listed which could be trigonal bipyramidal.

ii. In the absence of lone pairs, it must be dsp^3 or sp^3d. (An inner or valence d-orbital may be involved.)

EXAMPLE 2.14

a. Complete the following table:

	Hybrid type	Geometry
a.	———	Linear
b.	dsp^2	———
c.	———	Trigonal bipyramid
d.	———	Octahedral
e.	sp^2	———

b. Which of the sets of hybridised orbitals: sp, sp^2, sp^3, dsp^3, d^2sp^3, sp^3d^2 do(does) not maximise the angles between electron pairs?

c. Fluorine molecule is formed by the overlap of ______ .

d. Predict the shapes of the following species and describe the type of hybrid orbitals on the central atom.

i. $PbCl_4$ ii. N_2Cl_4 iii. PCl_3 iv. $BH_4^{\ominus}$ v. $SbF_6^{\ominus}$

e. How many σ and π bonds are present in a benzene molecule?

Sol.

a. i. sp ii. Square planar   iii. dsp^3

iv. d^2sp^3 or sp^3d^2 v. Trigonal planar

b. The sp^3d hybrids have 90° and 120° angles. Rearrangement of bond angles could produce angles greater that 90° but at the expense of the highly symmetrical structure.

c. Overlap of p–p orbitals.

d. i. Tetrahedral sp^3.

ii. Two pyramidal N-atoms, with sp^3 hybridisation on each, yield a non-planar molecule.

iii. Pyramidal, sp^3 (a lone pair occupies the fourth tetrahedral position).

iv. Tetrahedral, sp^3.

v. Octahedral, sp^3d^2.

e. 12 σ and 3π bonds.

MO Theory

EXAMPLE 2.15

a. What is the number of molecular orbitals obtained by mixing of two atomic orbitals?

b. i. Out of F_2 and OF, which of these molecules is (are) paramagnetic?

ii. Which should be more stable towards dissociation into atoms, OF or F_2 ?

c. Explain why $NO^{\oplus}$ is more stable towards dissociation into atoms than NO whereas $CO^{\oplus}$ is less stable than CO.

d. Predict whether $He_2^{\oplus}$ ion in its electronic ground state is stable toward dissociation into He and $He^{\oplus}$.

Sol.

a. Two

b. i. OF is paramagnetic, since it has one unpaired electron.

ii. OF should be more stable, since it has one fewer antibonding electron.

c. $NO^{\oplus}$ has lost an antibonding electron. Whereas $CO^{\oplus}$ has lost a bonding electron.

d. It should be stable because it has one more bonding electron than antibonding.

EXAMPLE 2.16

a. Compare and contrast the concepts of hybrid orbitals and molecular orbitals with respect to:

i. The number of atoms involved.

ii. The number of orbitals produced from a given number of ground state orbitals.

iii. The energies of the resulting orbitals with respect to one another.

b. Distinguish between non-bonding and antibonding orbitals.

Sol.

a.

Hybrid orbital	Molecular orbital
i. One central atom	i. More than one atom
ii. Same number	ii. Same number
iii. All the same	iii. Bonding orbitals lower in energy than antibonding orbitals

b. Non-bonding orbitals have the same energy as the atomic orbitals from which they are formed; antibonding orbitals have higher energies than the highest energy atomic orbitals from which they are formed.

EXAMPLE 2.17

a. State the bond order and indicate whether the species is paramagnetic.

i. B_2 ii. C_2 iii. N_2

iv. O_2 v. Br_2 vi. $Cl_2^{\oplus}$

b. Which of the following molecules has the highest bond order.

i. Ne_2 ii. F_2

c. Explain why N_2 has a greater dissociation energy than $N_2^{\oplus}$, whereas O_2 has a lower dissociation energy than $O_2^{\oplus}$.

d. The bonding σ 2*s* orbital has a higher energy than the antibonding σ^*1s orbitals. Why is the former a bonding orbital while the latter is an antibonding.

Sol. a.

	Bond order		Magnetic behaviour (P = paramagnetic, D = diamagnetic)
a.	B_2	1	P
b.	C_2	2	D
c.	N_2	3	D
d.	O_2	2	P
e.	Br_2	1	D
f.	Cl_2	1.5	P

b. i. Zero bond order

ii. One bond order

c. $N_2^{\oplus}$ has lost a bonding electron and so has been destabilised; $O_2^{\oplus}$ has lost an antibonding electron and has been stabilised.

d. The σ 2*s* orbital originates from atomic orbitals of higher energy than itself and so is bonding. The σ^*1s originates from atomic orbitals of lower energy than itself and so is antibonding. The relative energies of two σ orbitals are immaterial.

Consequence of Electronic Structure

EXAMPLE 2.18

a. Which properties of element depend on the electronic configuration of atoms and which do not?

b. Why the chemical properties of a group are similar? Why do they not have identical properties?

c. Account for the great chemical similarity of the lanthanoid elements (Z = 57 to 71).

d. Select the largest species in each group:

i. Ti^{+2}, Ti^{+3}, Ti ii. $F^{\ominus}$, Ne, $Na^{\oplus}$

e. Select the species with the largest IE in each group:

i. Na, K, Rb ii. F, Ne, Na

f. Which ion has the smallest radius: $Li^{\oplus}$, $Na^{\oplus}$, $K^{\oplus}$, Be^{+2}, Mg^{+2}?

g. Select among the element that has the lowest and highest IE: K, Ca, Se, B, Kr.

h. The ionic radii of S^{2-} and Te^{2-} are 184 and 220 pm, respectively. Predict the ionic radius of Se^{2-} and for P^{3-}.

i. In the ionic compound KF, the $K^{\oplus}$ and $F^{\ominus}$ have practically identical radii, about 134 pm each. Predict the relative atomic radii of K and F.

Sol.

a. Chemical and many physical properties depend on electronic configuration, but nuclear properties do not.

b. Their properties are similar because of similar outermost electronic configurations. The differences are due to their differences in size and the magnitude of shielding effect.

c. Their outermost two shells of electrons are alike ($-6s^2\,5d^1-$) or that configuration is very close to the ground state in stability. Moreover, all the lanthanides act as if they had this configuration to a great extent.

d. i. Ti ii. $F^{\ominus}$

e. i. Na ii. Ne

f. Be^{2+}, Be is a second period element, thus smaller than the higher period elements. The Be^{2+} ion is isoelectronic with $Li^{\oplus}$, but has a greater nuclear charge.

g. K has the lowest IE; Kr has the highest. IE increases along a period (→), being very small for alkali metals and very large for the noble gases.

h. Ionic radius of Se^{2-} is the average of those of S^{2-} and Te^{2-}, that is 202 pm. The actual value is 198 pm.

The expected radius of P^{3-} to be greater than that of S^{2-}, since two ions are isoelectronic but P has one less proton. Its actual radius is 212 pm.

i. The atomic radius of K should be much greater than 134 pm and that of F much smaller, since atomic cations are smaller than their parent atoms, while atomic anions are bigger than their parents. The observed atomic radius of K and F are 231 and 64 pm respectively.

EXAMPLE 2.19

Answer the following:

a. Select from each of the following groups, the one which has the largest radius:

i. Co, Co^{2+}, Co^{3+}	ii. S^{2-}, Ar, $K^{\oplus}$	iii. Li, Na, Rb
iv. C, N, O	v. Ne, Na, Mg	vi. La, Lu
vii. Cu, Ag, Au	viii. Ba, H_f	
ix. Mg, Na, $Na^{\oplus}$, Mg^{+2}, Al		

b. IE_1 of C is 11.2 eV. What would be the value of IE_1 of Si to be greater or less than this amount?

c. IE_1's of Al, Si and S and 6.0, 8.0 and 13.3 eV. What would be the value of IE_1 of P?

d. IE_1's of Li and K are 5.4 and 4.3 eV respectively. What would be the value of IE_1 of Na?

e. The IE's of Li, Be and C are 5.4, 9.3 and 11.3 eV. What would be the value of IE's of B and N?

f. Which of these elements have the lowest IE_1: Sr, As, Xe, S, F?

g. Select from each of the following group the element which has the largest IE.

i. Na, P, Cl	ii. He, Ne, Ar	iii. O, F, Ne

h. Arrange the species in each group in order of decreasing IE's and in each case explain the reason for the sequence.

i. K, Rb, Cs	ii. Be, B, C	iii. Cu, Ag, Au
iv. C, N, O	v. N, O, F	vi. K, Ca, Sc
vii. Na, Mg, Al	viii. Fe, Fe^{+2}, Fe^{+3}	ix. $K^{\oplus}$, Ar, $Cl^{\ominus}$

Explain why IE_1 of Cu is higher than that of K, whereas IE_2 are in reverse order.

Account for the difference in IE

i. between $K^{\oplus}$ and $Ca^{\oplus}$

ii. between $Cu^{\oplus}$ and $Zn^{\oplus}$

Ionisation potential is an old term for ionisation energy. Explain why the two are synonymous?

Sol.

a. i. Co (The others have the same nuclear charge, but less electrons.)

ii. S^{2-} (All have the same electronic configuration, but the S nucleus has the smallest positive charge.)

iii. Rb (It is in the largest period.)

iv. C (It is the farthest left in the periodic table.)

v. Na (It is the first element of a new period.)

vi. La (Lu is smaller because of lanthanoid contraction.)

vii. Au (Ag is almost the same size, because of the effect of the lanthanoid contraction on Au.)

viii. Ba (HF is much smaller because of the effect of the lanthanoid contraction.)

ix. Na (The size decreases along the period (→) and also as electrons are removed.)

Less (IE decreases down the group (↓) due to increasing atomic size, but other factors also play an important role.) The observed value is 8.1 eV.

c. It is difficult to remove an e^- from P than from S because of the added stability of the half-filled *p*-subshell. The observed value is 10.9 eV.

d. The IE of Na should be intermediate between that of Li and K. The IE of Na should be close to the arithmatic average of the two, or 4.9 eV. The observed is 5.1 eV.

e. Generally, IE increases along the period (→). However, there is a larger increase in IE from Li (Z = 3) to Be (Z = 4) than from Be to C (Z = 6). IE of B actually is less than that of Be, due to penetration effect in B. The observed IE of B is 8.3 eV.

N has a half-filled 2*p* subshell and should have extra stability for this reason. The increase in going from N (Z = 5) to C (Z = 6) is 3.0 eV, and the additional increase should be greater than this; thus, the IE of N should exceed 14.3 eV. The experimental value is 14.5 eV.

f. Sr (It is a metal.)

g. i. Cl (All of them belong to 3rd period and Cl is farthest to the right of the three elements.)

ii. He **iii.** Ne

h. i. K > Rb > Cs (Generally IE decreases down the group (↓)).

ii. C > Be > B (The 2*s* e^- is more difficult to remove than 2*p* (penetration effect).)

iii. Au > Cu > Ag (The lanthanoid contraction makes Ag and Au about equal in size, but Au has a much greater nuclear charge.)

iv. N > O > C (Due to stability of half-filled orbitals.)

v. F > N > O (The half-filed *p*-subshell of N imparts enough extra stability to make its IE > IE of O.)

vi. Sc > Ca > K (In each of these cases, a 4*s* e^- is being removed and the order is as shown.)

vii. Mg > Al > Na (It is more difficult to remove an e^- from Mg because the e^- being removed is a 3*s* e^- from a filled subshell. The 3*p* e^- of Al is easily removed. It is easiest to remove an e^- from Na because of its large size.)

viii. $Fe^{3+} > Fe^{2+} > Fe$ (All of them have same nuclear charge and the number of e^-'s increases in the order listed.)

ix. $K^{\oplus}$ > Ar > $Cl^{\ominus}$ (All have the same electronic configuration and the nuclear charge decreases in the order listed.)

i. i. Cu (Z = 29) ⇒ $3d^{10}\,4s^1$, $Cu^{\oplus} = 3d^{10}\,4s^o$, $Cu^{+2} = 3d^9\,4s^o$

ii. K (Z = 19) ⇒ $4s^1$, $K^{\oplus} = 4s^o$, $K^{+2} = 3p^5$

Cu has 10 more protons and 10 more e^-'s than does K, but due to imperfect screening effect of *de*$^-$'s, IE_1 of Cu > IE_1 of K and IE_2 for K involves the removal of an e^- from an octet ($3s^2\,3p^6$), whereas that of Cu involves the more easily ionised d^{10} configuration.

Hence, IE_2 of K > IE_2 of Cu.

j. i. $K^{\oplus}$ loses an e^- from its $3p^6$ subshell; $Ca^{\oplus}$ forms its 4*s* subshhell, which requires less energy.

Hence, IE_2 of $K^{\oplus}$ > IE_2 of $Ca^{\oplus}$.

ii. Zn (Z = 30) ⇒ $3d^{10}\,4s^2$, $Zn^{\oplus}$ ⇒ $3d^{10}\,4s^1$

Cu (Z = 29) ⇒ $3d^{10}\,4s^1$, $Cu^{\oplus}$ ⇒ $3d^{10}\,4s^0$

$Zn^{\oplus}$ loses an e^- from $4s^1$ more easily than $Cu^{\oplus}$ loses an e^- from $3d^{10}$.

Hence, IE_2 of $Cu^{\oplus}$ > IE_2 of $Zn^{\oplus}$.

k. The IE of an e^- in eV is numerically equal to IP in volts.

Note: If a particle being accelerated by a potential has a charge equal in magnitude to the charge on an e^-, the number of eV of energy is numerically equal to the potential in volts (V).

Bonding

Example 2.20

Give the decreasing order of the property mentioned against each of the following:

a. C_2H_2, BF_3, H_2O, NH_3, CH_4	(bond angle)
b. NH_3, $\overset{\ominus}{N}H_2$, $\overset{\oplus}{N}H_4$	(bond angle)
c. K – F, Li – Cl, Na – I, Br – H, F – H, C – H	(ionic character)
d. NH_3, PH_3	(bond angle)
e. NF_3, NH_3	(dipole moment)
f. CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4	(dipole moment)
g. MgO, CaO	(hardness)
h. HCl, HBr	(ionic character)
i. NO_2, $NO_2^{\oplus}$, $NO_2^{\ominus}$	(bond angle)
j. Cl_2, O_2, F_2, N_2	(bond strength)
k. O, N, F, Cl, S	(strength of H-bonding)
l. N_2, $N_2^{\oplus}$, $N_2^{\ominus}$, N_2^{2-}	(order of stability)
m. O_2^{2+}, O_2, $O_2^{\oplus}$, $O_2^{\ominus}$ O_2^{2-}	(order of stability)
n. N_2, F_2, O_2, H_2	(bond length)

Sol.

a. Refer to Chapter 1, Illustration 1.81, Question 11, part (h)

$$\underset{[sp,\ \text{linear}]}{CH\equiv CH\ (180^\circ)} > \underset{[sp^2,\ \text{planar}]}{BF_3\ (120^\circ)} > \underset{[sp^3,\ TH]}{CH_4\ (109.5^\circ)}$$

$$\underset{\left[\begin{array}{c} sp^3,\ \text{pyramidal} \\ \text{Repusion between} \\ lp \text{ and } bp \end{array}\right]}{\ddot{N}H_3\ (107^\circ)} > \underset{\left[\begin{array}{c} sp^3,\ \text{V-shape} \\ \text{Repusion between} \\ lp \text{ and } lp \end{array}\right]}{H_2\ddot{O}\text{:}\ (104.5^\circ)} >$$

b. $$\underset{[sp^3,\ TH]}{\overset{\oplus}{N}H_4(109^\circ)} > \underset{\left[\begin{array}{l} sp^3,\ \text{pyramidal} \\ \text{Repulsion between} \\ lp \text{ and } bp \end{array}\right]}{\ddot{N}H_3(107^\circ)} > \underset{\left[\begin{array}{l} sp^3,\ \text{V-shape} \\ \text{Repulsion between} \\ lp \text{ and } lp \end{array}\right]}{:\overset{\ominus:}{N}H_2(104^\circ)}$$

This is because all of them involve sp^3 hybridisation. The number of *lp*'s of electrons on N-atom are 0, 1 and 2 respectively. Greater the number of *lp*'s, greater is the repulsions on the *bp*'s and hence smaller is the angle.

c. K – F > Na – I > Li – Cl > F – H > Br – H > C – H.
(Apply Fajans' rule)

d. Refer to Section 1.16 (3), Point (v).

$NH_3 > PH_3$.

e. Refer to Illustration 2.15 (a).

$NH_3 > NF_3$.

f. Refer to Illustration 2.16.

$CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$.

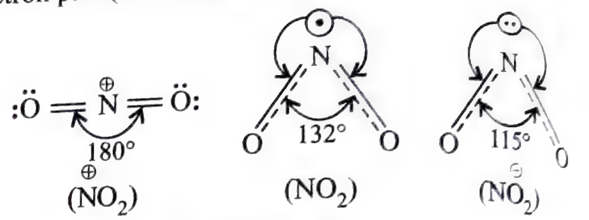
g. MgO > CaO (Hardness decreases down the 2nd group (↓) due to decreases in lattice energy.)

h. HCl > HBr (Apply Fajans' rule.)

i. Refer to Section 1.16 (3), Point (v).

$$\overset{\oplus}{NO_2} > NO_2 > \overset{\ominus}{NO_2}.$$

$\overset{\oplus}{NO_2}$ has no unshared electron and hence it is linear. NO_2 has one unshared electron while $NO_2^{\ominus}$ has one unshared electron pair (i.e. lone pairs of electrons).



j. N ≡ N > O = O > Cl – Cl > F – F

Triple bond strength > double bond strength > single bond strength.

Bond strength of F–F is less than that of Cl–Cl, due to repulsion between the non-bonding e^-'s present on each very small F-atoms.

k. F > O > N > S > Cl

Greater the EN and small size of the element, it forms stronger H-bonding.

l. Refer to Table 2.18.

$N_2 > N_2^{\oplus} > N_2^{\ominus} > N_2^{2-}$

m. Refer to Table 2.19.

$O_2^{2+} > O_2^{\oplus} > O_2 > O_2^{\ominus} > O_2^{2-}$

n. F_2 (F – F) > O_2 (O = O) > N_2 (N ≡ N) > H_2 (H – H)

[Bond length (pm)]	144	>	121	>	109	>	74

Bond length of single bond > double bond > triple bond.

Since the H-atom is very small size so bond length of single bond between H and H is the smallest.

Example 2.21

Answer the following:

a. How many σ, π and non-bonding electrons are present in:

i. P_4O_6 ii. P_4O_{10}

b. Which of the following are isostructural and isoelectonic?

$NO_3^{\ominus}$, CO_3^{2-}, $ClO_3^{\ominus}$, SO_3

c. Why CO_2 and SO_2 are not isostructural ?

d. Why PCl_5 dissociate to give PCl_3 and Cl_2, whereas SF_6 does not dissociate to give SF_4 and F_2 on heating?

e. Discuss the shapes of molecular orbitals formed by the combination of the following atomic orbitals.

i. $2p_z$ and $2p_z$ ii. $2p_x$ and $2p_x$

f. Why IF_7 dissociate to give $IF_2 + \frac{5}{2}F_2$ not $IF_2 + F_2$? Explain.

g. Why axial bonds of PCl_5 are longer than equatorial bonds?

h. $BH_4^{\ominus}$ and $\overset{\oplus}{N}H_4$ are isolobal. Explain.

i. Name the anion which is isostructural with BF_3.

j. Name the cation which is isostructural with CH_4.

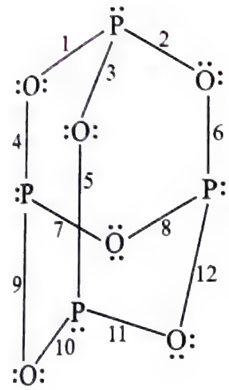
k. Which of the following alkali metal chlorides is expected to have the highest melting point.

i. LiCl ii. KCl iii. RbCl iv. NaCl

Sol.

a.

i.



(P_4O_6)

σ bonds = 12

π bond = Zero

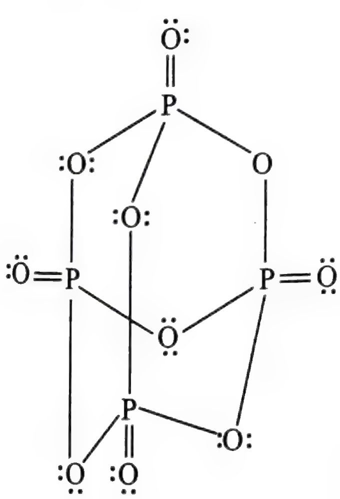
Each P has 1 *lp* of e^-'s.

Four P has 4 *lp*'s = 8 non-bonding e^-'s.

Each O-atom has 2 *lp*'s of e^-'s, 6 O-atom has 12 *lp*'s = 24 non-bonding e^-'s

$\therefore \sigma = 12, \pi = 0$, non-bonding e^-'s = 32

ii.



(P_4O_{10})

σ bonds = 12 + 4 = 16

π bond = 4

P-atom does not have *lp*'s of e^-'s.

Ten O-atom has 2 × 10 = 20 *lp*'s = 40 non-bonding e^-'s.

b. $NO_3^{\ominus}$ and CO_3^{2-} are isoelectronic and isostructural.

Number of e^-'s in $NO_3^{\ominus}$ = 7 + 24 + 1 = 32

Number of e^-'s in CO_3^{2-} = 6 + 24 + 2 = 32

Hence, they are isoelectronic.

Therefore, hybridisation of central atom in both cases is sp^2. Hence, they are isostructural also.

c. C in CO_2 is *sp* hybridised and is linear. S in SO_2 is sp^2 hybridised and is bent molecule.

d. Refer to Section 2.21.8 (Point 1) for PCl_5 and refer to Section 2.21.8 (5) for SF_6.

e. Refer to Figs. 2.74 and 2.75.

f. Refer to Section 2.21.12 [Point 7 (a)].

g. Refer to Section 2.21.8 (Point 1).

h. Both are sp^3 hybridised and have tetrahedral shape.

i. $NO_3^{\ominus}$ (Triangular planar).

j. $\overset{\oplus}{N}H_4$ (Tetrahedral).

k. Lattice energy ($\Delta_U H^{\ominus}$) decreases down the group (↓). Although $\Delta_U H^{\ominus}$ of LiCl is higher than that of NaCl but LiCl is covalent and NaCl is ionic in nature. After NaCl, $\Delta_U H^{\ominus}$ decreases as the size of alkali metal ion increases. As melting point depends upon lattice energy and ionic/covalent nature of the compounds, thus NaCl has the highest melting point.

EXAMPLE 2.22

Explain:

a. Which *d*-orbital is involved in:

i. sp^3d hybridisation ii. sp^3d^2 hybridisation

iii. dsp^2 hybridisation iv. sp^3d^3 hybridisation

b. Why H_2O is liquid while H_2S is gas ?

c. Why KHF_2 exists but $KHCl_2$ does not ?

d. Benzene ring contains alternate single and double bonds, yet all the C–C bonds are of equal length why?

e. Out of P–F, Cl–F, S–F and F–F bonds, which bond is the least ionic ?

Sol.

a. Refer to Section 2.21.11.

i. dz^2 ii. dx^2-y^2 and dz^2

iii. dx^2-y^2 iv. dxy, dyz, dxz

b. Due to intermolecular H-bonding in H_2O, association of H_2O molecules occurs but in H_2S there is no H-bonding.

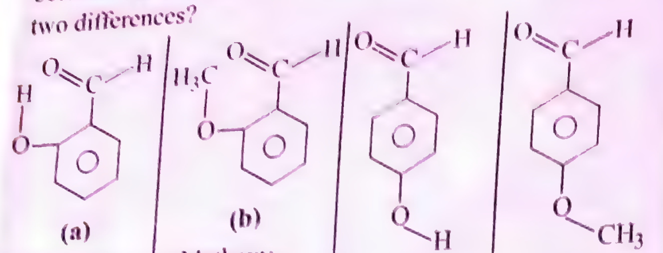
c. Refer to Section 2.23.11 (Point 6).

d. Due to resonance in benzene.

e. F–F is the least ionic or more covalent due to the zero EN difference in F–F atoms. Greater the difference in EN value of two atoms more ionic is the compound and vice versa.

EXAMPLE 2.23

How do you account for the difference in melting points between (a) and (b) between (c) and (d), and between these two differences?



(a) o-Hydroxy-benzaldehyde m.pt. = 266°C

(b) o-Methoxy-benzaldehyde m.pt. = 309°C

(c) p-Hydroxy-benzaldehyde m.pt. = 388°C

(d) p-Methoxy-benzaldehyde. m.pt. 273°C

Sol.

a. The crystal forces in (a) and (d) are largely van der Walls. Compounds (a) and (c) containing the polar–OH groups form H-bonding.

b. In (a), there is intramolecular H-bonding whereas in (c), it is intermolecular H-bonding which leads to increase in melting point of (c) as compared to (a) and (d).

c. In the absence of strong intermolecular H-bonding, the difference in m.pt. as compared with the reference substance (b) should be small. This is due to differences in the crystal structure or due to the van der Waals forces, which would be slightly larger for (b) than for (a) on account of the slightly increased molecular mass.

EXAMPLE 2.24

A plant virus was found to consist of uniform cylindrical particles 100 Å in diameter and 4000 Å long. The virus has a specific volume 0.314 $cm^3\,g^{-1}$. If the virus particle is considered to be one molecule, what is its molecular weight?

Sol. $V = \pi r^2 h = (3.14)\left(\frac{100\ \text{Å}}{2}\right)^2 (4000\ \text{Å}) = 3.14 \times 10^7\ (\text{Å})^3$

$$= 3.14 \times 10^7\ (\text{Å})^3 \left(\frac{10^{-8}\,\text{cm}}{\text{Å}}\right)^3 = 3.14 \times 10^{-17}\ \text{cm}^3$$

Therefore, the specific volume is 0.314 $cm^3\,g^{-1}$. of molecule. If e specific volume is 3.14×10^{-17} cm^3. The weight per molecule

$$= \left(\frac{1\,g}{0.314\ \text{cm}^3}\right)(3.14 \times 10^{-7}\ \text{cm}^3)$$

$$= 10^{-16}\ \text{g. molecule}^{-1}$$

Molecular weight of virus = $(10^{-6}\ \text{g molecule}^{-1})$

$$\left(\frac{6.02 \times 10^{23}\ \text{molecules}}{\text{mol.}}\right)$$

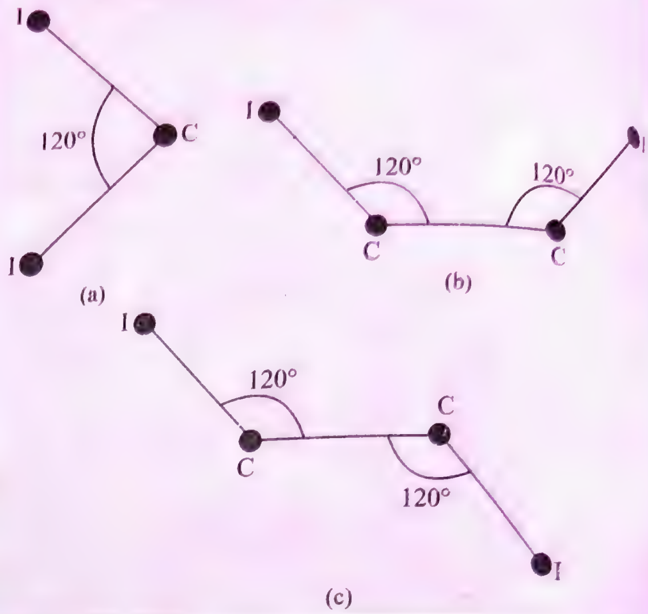
$$= 6.02 \times 10^7\ \text{g mol}^{-1}$$

EXAMPLE 2.25

Calculate the I–I distance in each of the isomeric compounds $C_2H_2I_2$ as shown below.

Given: Bond length of C – I ⇒ 210 pm

Bond length of C = C ⇒ 133 pm



Sol.

Note: (C = C) bond is sp^2 hybridised and planar with 120° angle.

a.

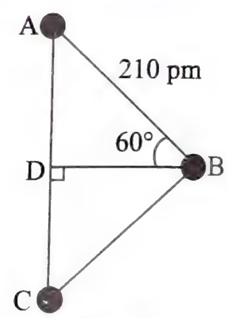


Fig. (a)

The I–I distance (Fig. a) $(\overline{AC}) = \overline{AD} + \overline{DC} = 2\overline{AD}$

C–I bond length $(\overline{AB}) = 210$ pm

In the 60° right angle triangle (ABD),

$2\overline{AD} = 2\ (210 \sin 60°) = \mathbf{364\ pm}$

b.

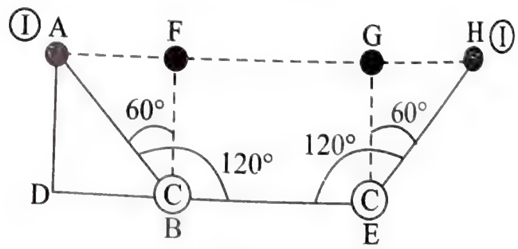


Fig. (b)

The I–I distance (Fig. b) = $\overline{AH} = \overline{AF} + \overline{GH} + \overline{FG}$

Now, $\overline{AF} = \overline{GH} = \overline{BD} = 210 \cos 60° = 105$ pm.

$\overline{FG}$ is the C=C double bond distance = 133 pm.

Thus, $\overline{AH} = 105 + 133 + 105 = 343$ pm.

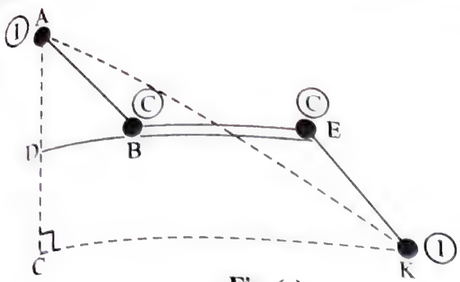


Fig. (c)

The I–I distance (Fig. c) = AK, the hypotenuse or right angle triangle ACK.

The legs of the triangle ACK are AC and CK.

AC = 364 pm (as calculated in part (a) above)

$\overline{CK} = \overline{AH}$ (as calculated in part (b) above) = 343 pm

Then, $\overline{AK} = \sqrt{(\overline{CK})^2 + (\overline{AC})^2}$

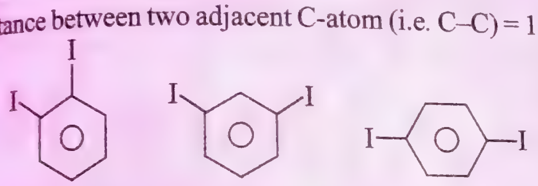
$= \sqrt{(343)^2 + (364)^2} = 500$ pm

Example 2.26

Calculate the I–I distance in each of the three isomeric diiodobenzenes. Assume that the ring is a regular hexagon and that each C–I bond lies on a line through the centre of the hexagon.

Given: C – I bond length = 210 pm.

The distance between two adjacent C-atom (i.e. C–C) = 140 pm.

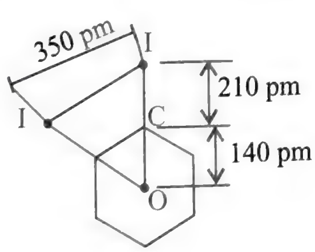


(a) (b) (c)

Sol. The distance from the centre of the hexagon to any corner (apex) = 140 pm.

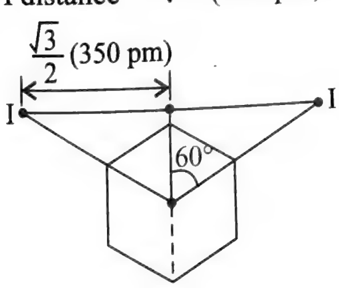
Since the hexagon is regular, the lines from the centre to two adjacent apices form an equilateral triangle.

a. The distance from the centre of the hexagon to an I-atom = OC + CI = (140 + 210) = 350 pm.

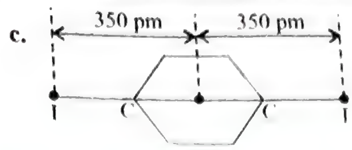


b. Half the I–I distance is $\frac{\sqrt{3}}{2}$ (350 pm).

Therefore I–I distance = $\sqrt{3}$ (350 pm) = 606 pm



c.



I–I distance = 2 (350 pm) = 700 pm

Example 2.27

Enthalpies of hydrogenation of ethene (C_2H_4) and benzene (C_6H_6) are –136.68 and 205.65 kJ mol^{-1} respectively. Calculate the resonance energy of benzene.

a. $C_2H_{4(g)} + H_{2(g)} \longrightarrow C_2H_6, \Delta H_1 = -136.68$ kJ mol^{-1}

b. $C_6H_{6(l)} + 3H_{2(g)} \longrightarrow C_6H_{12}, \Delta H_2 = -205.65$ kJ mol^{-1}

Sol. If benzene (C_6H_6) had three isolated (C = C) double bonds, $\Delta H^{\ominus}$ hydrogenation would be close to three times ΔH hydrogenation of ethene ($H_2C = CH_2$), with one double bond, i.e. $-136.68 \times 3 = -410.04$ kJ mol^{-1}.

$\Delta H^{\ominus}$ hydrogenation of benzene = – 205.65 kJ mol^{-1}

Hydrogenation of benzene is less exothermic by:

Resonance energy = $\Delta H^{\ominus}$ hydrogenation of C_6H_6

– $\Delta H^{\ominus}$ hydrogenation of 3 times of C_2H_4

= – 205.65 – (–410.04) kJ mol^{-1}

= 204.39 kJ mol^{-1}

It means that benzene has been stabilised by 204 kJ mol^{-1}.

Example 2.28

Select the species which is best described to the right.

a.	Cl_2, Br_2, I_2	(has the lowest boiling point)
b.	Cl, Ar, K	(has the smallest IE)
c.	CH_4, NH_3, HF	(has the highest boiling point)
d.	CO_2, NH_3, CO	(has zero dipole moment)
e.	HOI, HOBr, HOCl	(is the weakest acid)

Sol.

a. Cl_2 has the fewest electrons, therefore least van der Waals forces.

b. K is metal, thus smallest IE.

c. HF has H-bonding, the largest intermolecular force.

d. CO_2 has polar bonds, but CO_2 is linear, and the bond moments cancel.

e. In HOI, I is least EN; it pulls electrons least, leaving a greater fraction of the O electrons to bond with the H atom.

Example 2.29

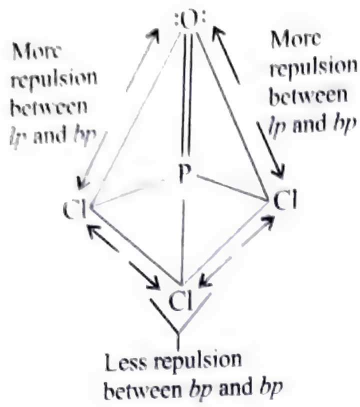
a. The Cl–O bond distance in $ClO_4^{\ominus}$ is 144 pm. What do you conclude about the structure of this ion?

b. The $POCl_3$ molecule has the shape of an irregular tetrahedron with the P atom located centrally. The Cl–P–Cl angle is found to be 103.5°. Give a qualitative explanation for the deviation of this structure from a regular tetrahedron.

Sol.

a. There must be considerable double bond character in the bonds.

b. The Lewis structure for $POCl_3$ would show some double bond character between P and O. (P is allowed to exceed the octet because of the availability of $3d$ orbitals).



The increased e^- density in the P = O bond would make the intrinsic repulsion between the P=O bond and a P–Cl bond greater than between two (P–Cl) bonds.

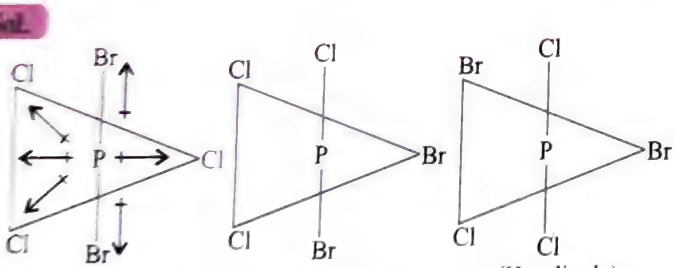
Thus, the Cl–P–Cl angle is lowered and the Cl–P = O angle is raised, as compared to regular tetrahedron.

Hybridisation

EXAMPLE 2.30

Draw all geometrical isomers of PBr_2Cl_3 molecule. State which isomer(s) have no dipole moment.

Sol.



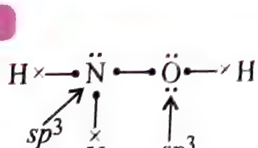
(No dipole) ($\mu = 0$) (Has dipole) ($\mu \neq 0$) (Has dipole) ($\mu \neq 0$)

EXAMPLE 2.31

Write electron dot structures and describe the geometry of the following molecules:

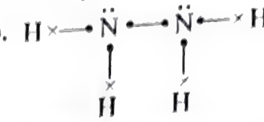
a. NH_2OH (Hydroxylamine)
b. NH_2NH_2 (Hydrazine)
c. CH_3COCl (Acetyl chloride)
d. $CH_2 = NH$ (Methylenamine)

Sol.

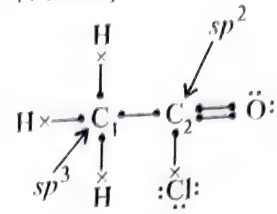
a. 

i. Due to one *lp* of e^- and three *bp*'s, N-atom is sp^3 hybridised but pyramidal in shape.

ii. Due to two *lp*'s of e^-'s and two *bp*'s, O-atom is hybridised but bent about the O-atom.

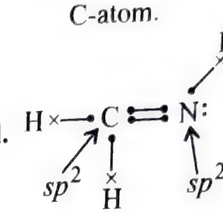
b. 

[Both N atoms are sp^3 hybridised and pyramidal about N-atom.]

c. 

i. C^1 is sp^3 hybridised and is tetrahedral in shape.

ii. C^2 is sp^2 hybridised and is trigonal planar about C-atom.

d. 

Both C and N atoms are sp^2 hybridised and are planar about C and N atoms.

EXAMPLE 2.32

a. Reduce the hybridisation, geometry and shape of the following:

i. CH_2^{2+} ii. $Br_3^{\ominus}$ iii. $ClO_3^{\oplus}$
iv. F_2SeO v. $IO_2F_2^{\ominus}$

b. Either of the hybridisations (i) dsp^2 and (ii) sp^3d^2 of a central atom can lead to a square planar molecule. Give one example of each.

Sol.

a. i. CH_2^{2+}

$$H = \frac{1}{2}(V + M - \text{no. of +ve charge})$$

$$= \frac{1}{2}(4 + 2 - 2) = 2 = sp$$

The molecule is linear. There will be no multiple bonding, since H-atoms have no orbitals available and C-atom has lost the extra electrons.

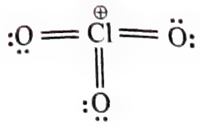
ii. $Br_3^{\ominus}$:Br̈ — Br̈: — Br̈:

$$H = \frac{1}{2}(V + M + \text{no. of –ve charge})$$

$$= \frac{1}{2}(7 + 2 + 1)$$

$$= 5 = sp^3d = \text{Tbp}$$

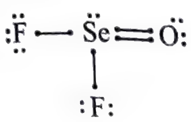
$BrO_3^{\ominus}$ has Tbp geometry but due to the presence of three *lp*'s, it is linear in shape.

iii. $ClO_3^{\oplus}$ 

$H = \frac{1}{2}(V + M - \text{no. of +ve charge})$

$= \frac{1}{2}(7 + 0 - 1) = 3 = sp^2 = \text{Planar}$

$ClO_3^{\oplus}$ is unstable ion, (Cl = O) bonding is expected.

iv. F_2SeO 

$H = \frac{1}{2}(V + M) = \frac{1}{2}(6 + 2) = 4 = sp^3 = \text{TH}$

F_2SeO has tetrahedral geometry but due to the presence of one *lp*, it has pyramidal in shape. This structure is analogous to SO_3^{2-}.

v. $IO_2F_2^{\ominus}$

$H = \frac{1}{2}(V + M + \text{no. of -ve charge})$

$= \frac{1}{2}(7 + 2 + 1) = 5 = sp^3d$

It has sp^3d hybridisation with Tbp geometry but due to the presence of one *lp* of e^-'s it has see-saw shape.

b. i. $[Ni(CN)_4]^{2-}$

ii. $:\ddot{X}eF_4$

Molecular Orbital Theory

EXAMPLE 2.33

State the bond order and indicate whether the species is paramagnetic:

a. $CN^{\oplus}$ b. CN c. $CN^{\ominus}$ d. NO

Sol.

a. $CN^{\oplus}$: Total number of e^-'s = 6 + 7 – 1 = 12

Remaining $p\ e^-$'s = 12 – 8 = 4

$N_b = 4, N_a = 0$

Bond order $= \frac{1}{2}(4 - 0) = 2$

Number of unpaired e^-'s = 0; therefore, diagmagnetic.

b. CN: Total electrons = 6 + 7 = 13

Remaining $p\ e^-$'s = 13 – 8 = 5

$N_b = 5, \quad N_a = 0$

Bond order $= \frac{1}{2}(5 - 0) = 2.5$

Number of unpaired e^-'s = 1; therefore, paramagnetic.

c. $CN^{\ominus}$: Total electrons = 6 + 7 + 1 = 14

Remaining $p\ e^-$'s = 14 – 8 = 6

$N_b = 6, \ N_a = 0$

Bond order $= \frac{1}{2}(6 - 0) = 3$

Number of unpaired e^-'s = Zero; therefore, diamagnetic.

d. NO: Total electrons = 7 + 8 = 15

Remaining $p\ e^-$'s = 15 – 8 = 7

Bond order $= \frac{1}{2}(6 - 1) = 2.5$

Number of unpaired e^-'s = 1; therefore, paramagnetic.

EXAMPLE 2.34

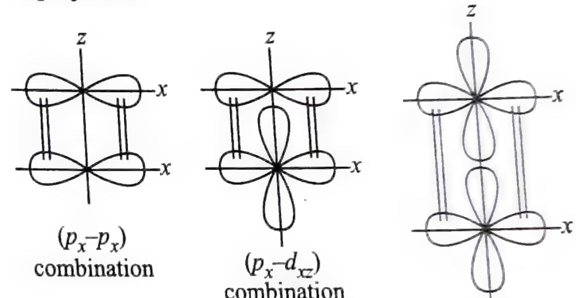
If the internuclear axis in the diatomic molecule AB is designated as the *z*-axis, what are the various pairs of *s*, *p* or *d* atomic orbitals that can be combined to from (a) π_x and (b) π_y orbitals?

Sol.

a. $(p_x, p_x), (p_x, d_{xz}), (d_{xz}, d_{xz})$

b. $(p_y, p_y), (p_y, d_{yz}), (d_{yz}, d_{yz})$

The figures below indicate the combination in *xz*-projection.



$(p_x–p_x)$ combination $(p_x–d_{xz})$ combination $(d_{xz}–d_{xz})$ combination

EXAMPLE 2.35

Make a table giving (i) number of orbitals with a given energy, (ii) maximum number of electrons per orbital and (iii) maximum number of electrons at a given energy for the following types of orbitals:

a. *s* b. *p* c. sp^2 d. sp^3

e. σ f. σ* g. π*

Sol.

	(i)	(ii)	(iii)
a.	1	2	2
b.	3	2	6
c.	3	2	6
d.	4	2	8
e.	1	2	2
f.	1	2	2
g.	2	2	4

EXAMPLE 2.36

When 2*s* orbital overlaps with $2p_x$ or $2p_y$ orbital (assumin[g] Z-axis as the internuclear axis), there is a partial overlap, an[d] they do not form any MO. Explain why?

Sol. 2s orbital wave function has same sign throughout but $2p_x$ or $2p_y$ orbital wave function has +ve sign in one lobe and –ve sign in the other lobe. The small (+) (+) overlap cancels the (+) (–) overlap which being equal in area but opposite in sign. (Refer to Fig. 2.72).

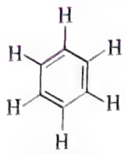
EXAMPLE 2.37

Compounds X and Y have similar structure with delocalization of π-electron system.

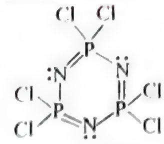
$(X)(CH)_n$ $\quad$ $(Y)(PNCl_2)_{n/2}$

If value of $n = 6$, then calculate the value of A/B, where 'A' is the total no. of σ bonds in compound (X) and (Y) and 'B' is total no. of π bonds in compounds X and Y.

Sol. (4) where $n = 6$

$X = (CH)_6 = C_6H_6$ = Benzene ⇒ 

(12σ, 3π)

$(Y) = (PNCl_2)_{6/2} = P_3N_3Cl_6 =$ 

(12σ, 3π)

Thus $A = (12 + 12) = 24\sigma$

$B = (3 + 6) = 6\pi$

Thus $A/B = \frac{24}{6} = 4$

EXAMPLE 2.38

Out of the following species, how many of the have fractional bond order.

(1) $CN^{\ominus}$	(2) $O_2^{\ominus}$	(3) C_2^{2-}	(4) B_2	(5) $He_2^{\oplus}$
(6) CO	(7) $N_2^{\ominus}$	(8) $NO^{\oplus}$	(9) $O_2^{\oplus}$	(10) C_2^{2+}

Sol. (4) Four species ($O_2^{\ominus}$, $He_2^{\oplus}$, $N_2^{\ominus}$ And $O_2^{\oplus}$)

	Species	Total no. of e^-'s	Remaining p e^-'s	Nb e^-'s	Na e^-'s	B.O.
1.	$CN^{\ominus}$	$(6+7+1)=14$	$14-8=6$	6	0	$\frac{1}{2}(6-0)=3$
2.	$O_2^{\ominus}$	$(8+8+1)=17$	$17-8=9$	6	3	$\frac{1}{3}(6-3)=1.5$
3.	C_2^{2-}	$(6+6+2)=14$	$14-8=6$	6	0	$\frac{1}{2}(6-3)=0$
4.	B_2	$(5+5)=10$	$10-8=2$	2	0	$\frac{1}{2}(2-0)=1$
5.	$He_2^{\oplus}$	$(2+2-1)=3$	—	2	1	$\frac{1}{2}(2-1)=0.5$
6.	CO	$(6+8)=14$	$14-8=6$	6	0	$\frac{1}{2}(6-0)=3$
7.	$N_2^{\ominus}$	$(7+7+1)=15$	$15-8=7$	6	1	$\frac{1}{2}(6-1)=2.5$
8.	$NO^{\oplus}$	$(7+8-1)=14$	$14-8=6$	6	0	$\frac{1}{2}(6-0)=3$
9.	$O_2^{\oplus}$	$(8+8-1)=15$	$15-8=7$	6	1	$\frac{1}{2}(6-1)=2.5$
10.	C_2^{2+}	$(6+6-2)=10$	$10-8=2$	2	0	$\frac{1}{2}(2-0)=1$

EXAMPLE 2.39

Consider the following compounds.

(1) $Al(OH)_3$ (2) $AsBr_4^{\oplus}$ (3) BeI_2 (4) $AlCl_3$ (5) $BrO_2^{\oplus}$
(6) $NO_2^{\ominus}$ (7) $IBr_4^{\ominus}$ (8) IF_5 (9) XeO_2F_2 (10) $NH_2^{\ominus}$

If a, b and c are total number of compounds in which central atom uses all three p-orbitals, only two p-orbitals and only one p-orbitals in hybridization respectively.

Then value of "$(a + c - b)$" is:

Sol. (2)

(1) sp^2 (2) sp^3 (3) sp (4) sp^2 (5) sp^2
(6) sp^2 (7) sp^3d^2 (8) sp^3d (9) sp^3d (10) sp^3

Compounds in which a = (2), (7), (8), (9) and (10)
= Total compounds = 5

Compounds in which b = (1), (4), (5), (6)
= Total compounds = 4

Compounds in which c = (3),
= Total compounds = 1

$\therefore$ $(a + c - b) = 5 + 1 - 4 = 2$

EXAMPLE 2.40

Out of the following species, the total number of species which have $(p\pi - p\pi)$ back bond or $(p\pi - d\pi)$ back bond are:

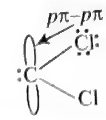
(1) CO (2) CCl_2 (Singlet) (3) $CBr_3^{\ominus}$
(4) CH_3NCS (5) Cl_2O (6) H_4SiO_4 (7) $(CH_3)_2O$
(8) $(SiH_3)_2O$ (9) $N(SiH_3)_3$

Sol. (7) Seven compounds (1 to 3, 5, 6 and 8, 9)

Back bonding is absent in (4)(CH_3NCS) and (7) [$(CH_3)_2O$]

(1) $:C\equiv O$
sp, $p\pi–p\pi$

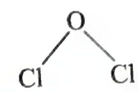
(2)



Vacant p-orbital
(Singlet with opposite spin) sp^2

(4) $CH_3–N=C=S$
no back bond.

(5)



EXAMPLE 2.41

Out of the following species, the total number of species which have symmetrical electron distribution in their HOMO (Highest Occupied Molecular Orbital) and also paramagnetic are:

(1) C_2^{2-} (2) B_2 (3) O_2 (4) N_2^{2-}
(5) C_2 (6) $N_2^{\oplus}$ (7) O_2^{2-}

Sol. (4) Four species (B_2, O_2, N_2^{2-} and $N_2^{\oplus}$)

Species	No. of e^-'s	No. of e^-'s remaining	No. of e^-'s in HOMO	Unpaired e^-'s and magnetic property
B_2	$5 + 5 = 10$	$10 - 8 = 2$	1 1 $\pi 2p_x$ $\pi 2p_y$ Symmetrical distribution	2, P
O_2	$8 + 8 = 16$	$16 - 8 = 8$ $6e^-$ in bonding $\sigma 2p_z$, $\pi 2p_x$ and $\pi 2p_y$	$2e^-$'s in 1 1 $\pi^* 2p_x$ $\pi^* 2p_y$ Symmetrical distribution	2, P
N_2^{2-}	$7 + 7 + 2 = 16$	$16 - 8 = 8$ $6e^-$ in bonding $\pi 2p_x$, $\pi 2p_y$ and $\sigma 2p_z$	$2e^-$'s in 1 1 $\pi^* 2p_x$ $\pi^* 2p_y$ Symmetrical distribution	2, P
$N_2^{\oplus}$	$7 + 7 - 1 = 13$	$13 - 8 = 15$ $4e^-$'s in bonding $\pi 2p_x$ and $\pi 2p_y$	$1e^-$ in 1 $\sigma 2p_z$ Symmetrical distribution	1, P

In C_2^{2-}, C_2 and O_2^{2-}, there is symmetrical electronic distribution in their HOMO, but all are diamagnetic

Example 2.42

Out of the following molecules, the total number of molecules which can form H-bond among themselves.

(1) HCHO	(2) HCOOH	(3) NH_2OH
(4) H_4SiO_4	(5) $NH(CH_3)_2$	(6) $B(OCH_3)_3$
(7) HCN	(8) SiH_3OH	(9) CH_3CONH_2

Sol. (7) Seven molecules (2 to 5 and 7 to 9) form H-bonds. Molecules (1 and 6 do not form H-bond)

Example 2.43

Out of the following species, the total number of species which can act as Lewis acid are:

(1) CO_2	(2) $SiCl_4$	(3) CH_4
(4) HCHO	(5) BF_3	(6) $TiCl_4$
(7) $(CH_3)_3Al$	(8) $(C_2H_5)_3N$	(9) $CH_3^{\oplus}$

Sol. (7) Seven species (CO_2, $SiCl_4$, HCHO, BF_3 $TiCl_4$, $(C_2H_5)_3Al$ and $CH_3^{\oplus}$) acts as Lewis acid.

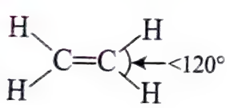
CH_4 and $(CH_3)_3Al$ does not act as Lewis acid

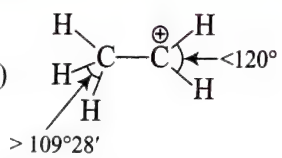
Example 2.44

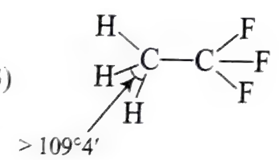
Out of the following compounds, the total number of compounds which have H–C–H bond angles greater than 109°28′ and less than 120° are:

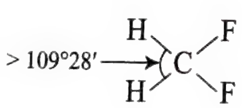
(1) C_2H_4	(2) $CH_3CH_2^{\oplus}$	(3) $H_3C–CF_3$
(4) H_2CF_2	(5) $H_3C–F$	(6) CH_4

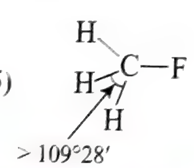
Sol. (4) Four compounds (1, 3, 4 and 5)

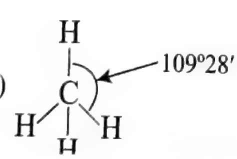
(1) 

(2) 

(3) 

(4) 

(5) 

(6) 

Example 2.45

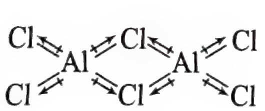
Out of the following compounds, the total number of non polar compounds are:

(1) ClF	(2) Al_2Cl_6	(3) S_2F_2	(4) SF_2
(5) SF_4	(6) PCl_2F_3	(7) PCl_3F_2	(8) ClF_3
(9) XeF_4	(10) I_2Cl_6	(11) BF_3	

Sol. (5) Five compounds (Al_2Cl_6, XeF_4, I_2Cl_6, PCl_3F_2 and BF_3) are non-polar.

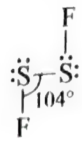
(1) $:\ddot{\underset{..}{Cl}}\rightarrow F$

sp^3, geometry = T.H.
Shape = Linear and polar

(2) 

(All vectors cancel out)

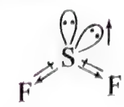
$\mu = 0$, non-polar

(3) 

$\mu \neq 0$, polar

(4) $:\ddot{S}F_2$

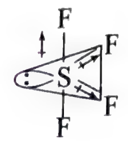
sp^3, G = T.H. shape Lin



$\mu \neq 0$, polar

(5) $:SF_4$

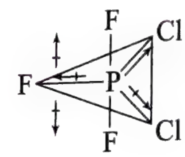
sp^3d, G = Trigonal bipyramid
Shape = Trigonal pyramid



$\mu \neq 0$, polar

(6) PCl_2F_3,

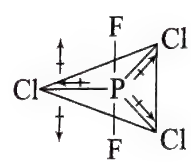
sp^3d, Geometry and shape T.b.p.



$\mu \neq 0$, polar.

(7) PCl_3F_2;

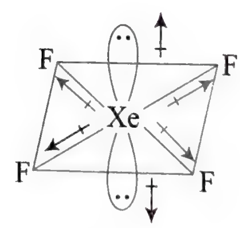
sp^3d, Geometry and shape = T.b.p.



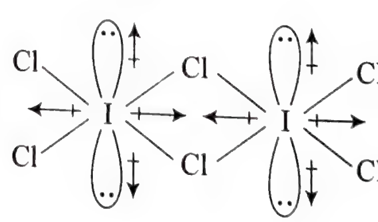
All vectors cancel out.
$\mu = 0$, non-polar

(8) $:\ddot{X}eF_4$

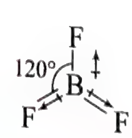
sp^3d^2, Geometry = Octahedral
Shape = Square planar



All vectors cancel out
$\mu = 0$ non-polar

(9) 

Planar structure
All vectors cancel out.
$\mu = 0$, non-polar

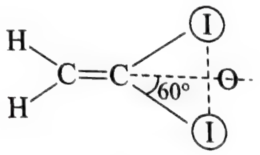
(10) 

sp^2, planar,
All vectors cancel out,
$\mu = 0$, Non-polar

Example 2.46

Calculate the (I – I) distance for the compounds CH_2Cl_2, if (C – I) bond length is 2.30Å.
(Given sin 60° = 0.86)

Sol. CH_2CI_2 is sp^2 hybridised and thus (I – C – I) bond angle is 120°.



(In ΔICO, angle ICO = 60° and angle IOC = 90°)

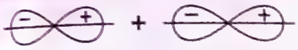
$$\frac{IO}{CI} = \sin 60°$$

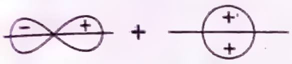
$$\therefore IO = CI \sin 60°$$
$$= 2.30 \times 0.86$$
$$= 1.987 \text{ Å}$$
$$\approx 2\text{Å}$$

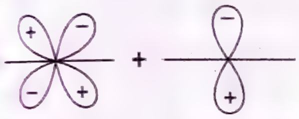
$$d(I-I) = 2 \times IO \approx 2 \times 2 \approx 4\text{Å}$$

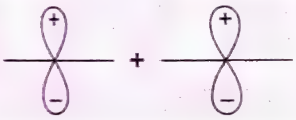
EXAMPLE 2.47

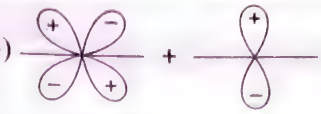
Some arrangement of atomic orbitals are given below:

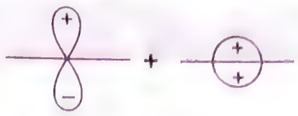
(1) 

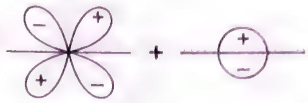
(2) 

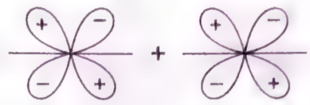
(3) 

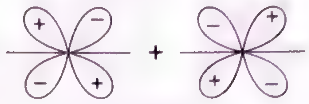
(4) 

(5) 

(6) 

(7) 

(8) 

(9) 

If A, B and C are number of arrangements which give bonding molecular orbitals, anti-bonding molecular orbitals and non bonding molecular orbitals respectively. Then the value of $(A + B - C)$ is:

Sol. (5) Bonding molecular orbitals (positive overlap) (i.e., A) = 4 (i.e., 2, 3, 4 and 7).

Anti-bonding molecular orbitals (negative overlap) (i.e. B) = 3 (i.e. 1, 5 and 8). Non-bonding molecular orbitals (zero overlap) (i.e. C) = 2 (i.e. 6 and 7).

$\therefore (A + B - C) = (4 + 3 - 2) = 5$

Exercises

Single Correct Answer Type

Chemical Bonding

1. Which of the following is the most ionic?
   (1) P_4O_{10} (2) MnO
   (3) CrO_3 (4) Mn_2O_7
2. Among LiCl, $BeCl_2$, BCl_3 and CCl_4, the covalent bond character varies as
   (1) $LiCl < BeCl_2 > BCl_3 > CCl_4$
   (2) $LiCl > BeCl_2 < BCl_3 < CCl_4$
   (3) $LiCl < BeCl_2 < BCl_3 < CCl_4$
   (4) $LiCl > BeCl_2 > BCl_3 > CCl_4$
3. In a metallic crystal the
   (1) Valence electrons remain within the fields of influence of their own kernels
   (2) Valence electrons constitute a sea of mobile electrons
   (3) Valence electrons are localised between the two kernels
   (4) Kernels as well as the electrons move rapidly
4. Polarisation involves the distortion of the shape of an anion by an adjacently placed cation. In this context, which of the following statements is correct?
   (1) Maximum polarisation is brought about by a cation of high charge.
   (2) Minimum polarisation is brought about by a cation of low radius.
   (3) A large cation is likely to bring about a high degree of polarisation.
   (4) The polarising power of a cation is less than that of an anion.
5. Which of the following is required for the formation of an ionic bond?
   (1) An electron from the more electronegative element should be transferred to the less electronegative.
   (2) The total energy of the resulting molecule should be less than the total energy of the reactants.
   (3) The lattice energy of the resultant molecule should be as low as possible.
   (4) The ionic potential of the reactants should be identical.
6. $AlCl_3$ is covalent while AlF_3 is ionic. This can be justified on the basic of
   (1) The valence bond theory
   (2) Fajans' rules
   (3) The molecuar orbital theory
   (4) Hydration energy
7. Which of the following oxyacids of phosphorous are monoprotic (monobasic)?
   (1) H_3PO_4 (2) H_3PO_3
   (3) H_3PO_2 (4) $H_4P_2O_7$
8. Which of the following has greater bond length?
   (1) P—O (2) S—O
   (3) Cl—O (4) O=O
9. Which of the following has been arranged in order of increasing covalent character?
   (1) $KCl < CaCl_2 < AlCl_3 < SnCl_4$
   (2) $SnCl_4 < AlCl_3 < CaCl_2 < KCl$
   (3) $AlCl_3 < CaCl_2 < KCl < SnCl_4$
   (4) $CaCl_2 < SnCl_4 < KCl < AlCl_3$
10. Which of the following pairs have nearly identical values of bond energy?
    (1) O_2 and H_2 (2) N_2 and CO
    (3) F_2 and I_2 (4) O_2 and Cl_2
11. Which has maximum ionic mobility
    (1) $Li^{\oplus}$ (2) $Na^{\oplus}$
    (3) $K^{\oplus}$ (4) $Cs^{\oplus}$
12. In PO_4^{3-}, P–O bond order is
    (1) 1.25 (2) 2
    (3) –0.75 (4) –3
13. Which of the following has least covalent P–H bond?
    (1) PH_3 (2) P_2H_6
    (3) P_2H_5 (4) $PH_6^{\oplus}$
14. Which of the following diatomic molecules would be stabilised by the removal of an electron?
    (1) O_2 (2) $CN^{\ominus}$
    (3) N_2 (4) C_2
15. In which of the following species the bonds are non-directional?
    (1) NCl_3 (2) RbCl
    (3) $BeCl_2$ (4) BCl_3
16. Which contains both polar and non-polar bonds?
    (1) NH_4Cl (2) HCN
    (3) H_2O_2 (4) CH_4
17. The bond angle between two hybrid orbitals is 180°. The percentage *s*-character of hybrid orbital is between
    (1) 50 and 55% (2) 9 and 12%
    (3) 22 and 23% (4) 11 and 12%
18. Which type of bond is **not present** in HNO_2 molecule?
    (1) Covalent (2) Coordinate
    (3) Ionic (4) Both ionic and coordinate
19. KF combines with HF to form KHF_2. The compound contains the species
    (1) $K^{\oplus}$, $F^{\ominus}$ and $H^{\oplus}$ (2) $K^{\oplus}$, $F^{\ominus}$ and HF
    (3) $K^{\oplus}$ and $[HF_2]^{\ominus}$ (4) $[KHF]^{\oplus}$ and F_2
20. There is no S–S bond in
    (1) $S_2O_6^{2-}$ (2) $S_4O_6^{2-}$
    (3) $S_2O_3^{2-}$ (4) $S_2O_7^{2-}$

21. Angle between two hybridised orbital is 105° and hence the percentage of s-character in the hybridised orbital would be in the range

(1) 23–24% (2) 20–21%
(3) 50–55% (4) 11–12%

22. The octer rule is not valid for the molecule

(1) CO_2 (2) H_2O
(3) O_2 (4) CO

23. The total number of electrons that take part in forming the bond in N_2 is

(1) 2 (2) 4
(3) 6 (4) 10

24. The types of bonds present in $CuSO_4 \cdot 5H_2O$ are only

(1) Electrovalent and covalent
(2) Electrovalent and coordinate covalent
(3) Electrovalent, covalent and coordinate covalent
(4) Covalent and coordinate covalent

25. The bond between two indentical non-metal atoms has a pair of electrons:

(1) Unqually shared between the two
(2) Transferred fully from one atom to another
(3) With identical spins
(4) Equally shared between them

26. The number and type of bonds between two C-atoms in SrC_2 are

(1) $1\sigma, 1\pi$ (2) $1\sigma, 2\pi$
(3) $1\sigma, 1.5\pi$ (4) 1σ

27. Which species has the maximum number of lone pair of electrons on the central atom?

(1) $[ClO_3]^{\ominus}$ (2) XeF_4
(3) N_2O (4) $[I_3]^{\ominus}$

28. Among the following, electron-deficient compound is

(1) CCl_4 (2) PCl_5
(3) OF_2 (4) BCl_3

29. Which of the following does not follow the octet rule?

(1) CO_2 (2) PCl_3
(3) ICl (4) ClF_3

30. Which of the following does not have coordinate bonds?

(1) CO_3^{2-} (2) $H_3C{-}NC$
(3) CO (4) O_3

31. Which of the following bonds is the strongest?

(1) I – I (2) F – F
(3) H – H (4) O – O

32. When two atoms combine to form a molecule

(1) Energy is released
(2) Energy is absorbed
(3) Energy is neither released nor absorbed
(4) Energy may either be absorbed or released

33. Most favourable conditions for ionic bonding are

(1) Low charge on ions, large cations, small anions
(2) Low charge on ions, large cations, large anions
(3) High charge on ions, small cations, large anions
(4) High charge on ions, large cations, small anions

34. Which of the following is not a correct statement?

(1) Ionic compounds are electrically neutral.
(2) Boilling point of an ionic compound is more than a covalent compound.
(3) Melting point of a covalent compound is more than an ionic compound.
(4) Ionic compounds are soluble in polar solvent.

35. Element A has three electrons in the outermost orbit and B has six electrons in the outermost orbit. The formula of the compound will be

(1) A_2B_3 (2) A_2B_6
(3) A_2B (4) A_3B_2

36. The pair of elements which form ionic bond is

(1) C + Cl (2) H + F
(3) Na + Br (4) O + H

37. Lattice energy of an ionic compound depends upon

(1) Charge on the ion and size of the ion
(2) Packing of ions only
(3) Size of the ion only
(4) Charge on the ion only

38. The bonds present in N_2O_5 are

(1) Only ionic (2) Covalent and coordinate
(3) Only covalent (4) Covalent and ionic

39. Which of the following statements is correct for CO?

(1) A double bond between C and O atoms
(2) 1σ, 1π and 1 coordinate bond between C and O atoms
(3) One lone pair of electrons on each atom
(4) 1σ, 2π bonds between C and O atoms

40. Which of the following statement regarding valence bond theory (VBT) is not true?

(1) A molecule is considered to be a collection of atoms, and then interactions between different atoms is considered.
(2) For a molecule to be stable, the electrostatic attractions must predominate over the repulsion.
(3) The potential energy of a diatomic molecule is less than the sum of potential energies of free atoms.
(4) The net force of altration acting on the atoms in a molecule is not zero.

41. Correct statement about VBT is

(1) Each bond is formed by maximum overlap for its maximum stability.
(2) It represents localised electron modal of bonding.
(3) Most of the electrons retain the same orbital localisation as in a separate atom.
(4) All are correct.

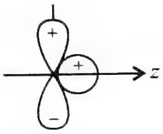
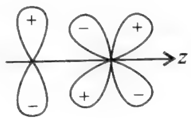
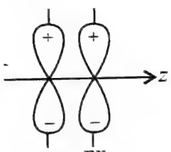
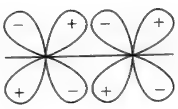
42. The strength of bonds formed by overlapping of atomic orbitals is in the order:

(1) $s-s > s-p > p-p$ (2) $s-s < p-p < s-p$
(3) $s-p < s-s < p-p$ (4) $p-p < s-s < s-p$

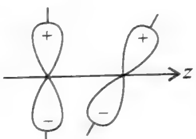
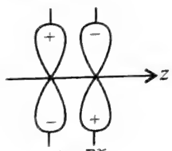
43. The nodal plane in the π-bond of ethene is located in:
(1) The molecular plane
(2) A plane parallel to the molecular plane
(3) A plane perpendicular to the molecular plane which bisects the (C – C) σ-bond at a right angle
(4) A plane perpendicular to the molecular plane which contains the (C – C) σ-bond

44. Which of the following statement is wrong?
(1) A σ-bond is shorter than a π-bond.
(2) Bond energies of σ and π bonds are of the order of 264 and 347 kJ mol^{-1}.
(3) Free rotation of atoms about a σ-bond is allowed but not in case of a π-bond.
(4) A σ-bond determines the direction between C-atoms but a π-bond has no primary effect which leads to bonding.

45. Which of the following is a positive overlap which leads to bonding?

(1) 
(2) 
(3) 
px px
(4) 

46. Which of the following is a zero overlap which leads to non-bonding?

(1) 
px py
(2) 
(3) 
px px
(4) All

Dipole Moment

47. Dipole moment of H_2O is 1.84 D. If the bond angle is 105° and O–H bond length is 0.94 Å, what is the magnitude of charge on the oxygen atom in water molecule?
(1) 2×10^{-10} esu (2) 3.28×10^{-10} esu
(3) 3.22×10^{-10} esu (4) 1.602×10^{-19} C

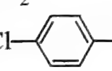
48. Diatomic molecule has a dipole moment of 1.2 D. If its bond is 1.0 Å, what fraction of an electronic charge exists on each atom?
(1) 11% (2) 20%
(3) 25% (4) None of these

49. The compound with no dipole moment is
(1) CH_3Cl
(2) CCl_4
(3) Methylene chloride (CH_2Cl_2)
(4) chloroform ($CHCl_3$)

50. The molecule which have zero dipole moment is
(1) CH_2Cl_2 (2) BF_3
(3) NF_3 (4) ClO_2

51. The critical temperature of water is higher than that of O_2 because the H_2O molecule has:
(1) A fewer electrons than O_2
(2) A dipole moment
(3) a V shape structure
(4) Two covalent bonds

52. The correct order of dipole moment is
(1) $CH_4 < NF_3 < NH_3 < H_2O$
(2) $NF_3 < CH_4 < NH_3 < H_2O$
(3) $NH_3 < NF_3 < CH_4 < H_2O$
(4) $H_2O < NH_3 < NF_3 < CH_4$

53. Among the following which is polar?
(1) CO_2 (2) SO_2
(3) $BeCl_2$ (4) Cl––Cl

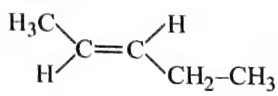
54. Which of the following is polar?
(1) NF_3 (2) BF_3
(3) SF_6 (4) SiF_4

55. The resultant dipole moment (μ) of two compounds NOF and NO_2F is 1.81 D and 0.47 D respectively. Which dipole moment do you predict?
(1) 1.81 D for NO_2F and 0.47 D for NOF
(2) 0.47 D for NO_2F and 1.81 D for NOF
(3) For both NO_2F and NOF, dipole moment (μ) is 1.81 D
(4) For both NO_2F and NOF, dipole moment (μ) is 0.47 D

56. In terms of polar character, the correct order is
(1) $H_2S > HF > H_2O > NH_3$ (2) $HF > H_2O > NH_3 > H_2S$
(3) $HF > H_2S > NH_3 > H_2O$ (4) $H_2S > NH_3 > H_2O > HF$

57. How many σ and π bonds are there in the molecule of tetracyano ethylene?
(1) 4σ, 14π (2) 5σ, 13π
(3) 8σ, 10π (4) 9σ, 9π

58. H_2O is dipolar, whereas BeF_2 is not. It is because
(1) EN of F > EN of O.
(2) H_2O involves H-bonding, whereas BeF_2 is a discrete molecule.
(3) H_2O is linear and BeF_2 is angular
(4) H_2O is angular and BeF_2 is linear

59. Which of the following hydrocarbons has the lowest dipole moment?
(1) 

(2) $H_3C - C \equiv C - CH_3$
(3) $H_3C - CH = C = CH_2$ (4) $H_3C - CH_2 - C \equiv CH$

60. Which of the following is the decreasing order of their dipole moments?
(1) $NH_3 > BF_3 > NF_3$ (2) $NH_3 > NF_3 > BF_3$
(3) $BF_3 > NH_3 > NF_3$ (4) $BF_3 > NF_3 > NH_3$

61. Which statement(s) is/are correct about dipole moment.
I. 1 Debye is equivalent to 3.33×10^{-30} Cm.
II. 1 Debye is equivalent to 10^{-18} esu.
III. SI unit of dipole moment is coulomb meter (Cm) ($1\ Cm = q \times d = 1.602 \times 10^{-19} \times 10^{-9}$ m).
IV. Dipole moment of a molecule is useful to explain the shape of a molecule and also to predict other properties of the molecule.
(1) I, II (2) I, III, IV
(3) I, II, III (4) All

62. Which of the following molecule(s) have dipole moment?
I. Trans-pent-2-ene **II.** *cis*-hex-3-ene
III. 2, 2-Dimethyl propane
IV. 2, 2, 3, 3-tetramethyl butane
(1) I, II (2) II, III
(3) I, III (4) I, IV

Hybridisation

63. The shapes of $PCl_4^{\oplus}$, $PCl_4^{\ominus}$ and $AsCl_5$ are respectively
(1) Square planar, tetrahedral and see-saw.
(2) Tetrahedral, see-saw and trigonal bipyramidal.
(3) Tetrahedral, square planar and pentagonal bipyramidal.
(4) Trigonal bipyramidal, tetrahedral and square pyramidal.

64. The $I_3^{\ominus}$ ion has
(1) Five equatorial lone pairs on the central I atom and two axial bonding pairs in a trigonal bipyramidal arrangement.
(2) Five equatorial lone pairs on the central I atom and two axial bonding pairs in a pentagonal bipyramidal arrangement.
(3) Three equatorial lone pairs on the central I atom and two axial bonding pairs in a trigonal bipyramidal arrangement.
(4) Two equatorial lone pairs on the central I atom and three axial bonding pairs in a trigonal bipyramidal arrangement.

65. In the reaction $2PCl_5 \rightleftharpoons PCl_4^{\oplus} + PCl_6^{\ominus}$, the change in hybridisation is from
(1) sp^3d to sp^3 and sp^3d^2 (2) sp^3d to sp^2 and sp^3
(3) sp^3d to sp^3d^2 and sp^3d^3 (4) sp^3d^2 to sp^3 and sp^3d

66. There are four species CO_2, $N_3^{\ominus}$, $NO_2^{\oplus}$ and $I_3^{\ominus}$. Which of the following statement is correct about these species?
(1) All are linear and having *sp* hybridisation of central atoms.
(2) All are linear but only CO_2, $N_3^{\ominus}$ and $I_3^{\ominus}$ have *sp* hybridisation on their central atom.
(3) All are linear but only CO_2, $N_3^{\ominus}$ and $\overset{\oplus}{NO_2}$ have *sp* hybridisation on their central atom.
(4) CO_2, $N_3^{\ominus}$ and $NO_2^{\oplus}$ are linear but $I_3^{\ominus}$ is not.

67. In the hybridisation of one *s* and one *p* orbitals, we get
(1) Two mutually perpendicular orbitals.
(2) Two orbitals at 180°.
(3) Two orbitals directed tetrahedrally.
(4) Three orbitals in a plane.

68. Which molecule is T or arrow (→) shaped.
(1) BeF_2 (2) BCl_3
(3) NH_3 (4) ClF_3

69. The hybridisation of the central atom in $ICl_2^{\oplus}$ is
(1) sp^3 (2) sp^2
(3) sp^2 (4) sp

70. The molecule that linear structure is
(1) CO_2 (2) NO_2
(3) SO_2 (4) SiO_2

71. The molecule which has pyramidal shape is
(1) PCl_3 (2) SO_3
(3) CO_3^{2-} (4) $NO_3^{\ominus}$

72. The compound which C uses in the sp^3 hybrid orbitals for bond formation is
(1) HCOOH (2) $(H_2N)_2CO$
(3) $(CH_3)_3COH$ (4) CH_3CHO

73. Which one of the following compounds has sp^2 hybridisation?
(1) CO_2 (2) SO_2
(3) N_2O (4) CO

74. CO_2 has same geometry as
(1) $HgCl_2$ (2) NO_2
(3) $SnCl_2$ (4) CH_4

75. In which pair of species, both species do have the similar geometry?
(1) CO_2, SO_2 (2) NH_3, BH_3
(3) CO_3^{2-} (4) SO_4^{2-}, $ClO_4^{\ominus}$

76. The geometry and the type of hybrid orbital present about the central atom in BF_3 is
(1) Linear, *sp* (2) Trigonal planar, sp^2
(3) Tetrahedral, sp^3 (4) Pyramidal, sp^3

77. SF_2, SF_4 and SF_6 have the hybridisation at sulphur atom respectively as:
(1) sp^2, sp^3, sp^2d^2 (2) sp^3, sp^3, sp^3d^2
(3) sp^3, sp^3d, sp^3d^2 (4) sp^3, spd^2, d^2sp^3

78. Two types FXF angles are present in which of the following molecule (X = S, Xe, C)?
(1) SF_4 (2) XeF_4
(3) SF_6 (4) CF_4

79. A σ-bonded molecule MX_3 is T-shaped. The number of non-bonding pairs of electrons is
(1) 2 (2) 1
(3) 0
(4) Can be predicted only if atomic number of M is known

80. In $\overset{\oplus}{NH_4}$ and OF_2, the hybridisation of central atom respectively are

(1) sp^3, sp^2 (2) sp^3, sp^3
(3) sp^3d, sp^3d (4) sp^3d, sp^3

81. Hybridisation involves
(1) Orbitals of same atom with slightly different energies
(2) Orbitals of different atoms but with equal energies
(3) Orbitals of different atoms with different energies
(4) Orbitals of same atoms with exactly equal energies

82. AsF_5 molecule is sp^3d hybridised and is trigonal bipyramidal (Tbp) shape. Which d-orbital is involved in sp^3d hybridisation.
(1) dx^2-y^2 (2) dz^2
(3) dxy (4) dzx

83. $[PtCl_4]^{2-}$ molecule is dsp^2 hybridised and is square planar. Which d-orbital is involved in dsp^2 hybridisation.
(1) $dx^2 - y^2$ (2) dz^2
(3) dxy (4) dyz

84. SeF_6 is sp^3d^2 hybridised and is octahedral (OH). Which d orbitals are involved in hybridisation.
(1) $dx^2 - y^2, dxy$ (2) $dx^2 - y^2, dz^2$
(3) dxy, dyz (4) dz^2, dxy

85. IF_7 is sp^3d^3 hybridised and is Pbp (pentagonal bipyramid). Which d orbitals are involved in hybridisation.
(1) dxy, dyz, dxz (2) $dx^2 - y^2, dz^2, dxy$
(3) $dx^2 - y^2, dyz, dxz$ (4) $dx^2 - y^2, dz^2, dyz$

86. In a regular octahedral molecule, SF_6, the number of F–M–F bonds at 180° is
(1) 2 (2) 3
(3) 4 (4) 6

87. The maximum number of 90° angles between bp-bp of electrons is observed in:
(1) sp^3d hybridisation (2) dsp^3 hybridisation
(3) dsp^2 hybridisation (4) sp^3d^2 hybridisation

88. Among the following ions, the $p\pi$–$d\pi$ overlap is present in:
(1) $NO_3^{\ominus}$ (2) $PO_4^{\ominus}$
(3) CO_3^{2-} (4) $NO_2^{\ominus}$

89. Which of the following have distorted octahedral structure?
(1) SF_6 (2) $PF_6^{\ominus}$
(3) SiF_6^{2-} (4) XeF_6

90. Sulphur reacts with chlorine in 1:2 ratio and forms X. Hydrolysis of X gives a sulphur compound Y. What is the hybridisation state of central atom in the compound.
(1) sp^3 (2) sp^2
(3) sp (4) dsp^2

H-Bonding

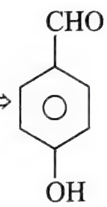
91. Orthonitrophenol is steam volatile but paranitrophenol is not because
(1) Orhtonitrophenol has intramolecular hydrogen bonding while paranitrophenol has intermolecular hydrogen bonding.
(2) Both ortho and paranitrophenol have intramolecular hydrogen bonding.
(3) Orthonitrophenol has intermolecular hydrogen bonding and paranitrophenol has intramolecular hydrogen bonding.
(4) van der Waals forces are dominant in orthonitrophenol.

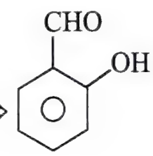
92. Which of the following compounds has the least tendency to form H-bonds?
(1) HF (2) HCl
(3) H_2O (4) NH_3

93. Which one of the following molecule will form a linear polymeric structure due to H-bonding?
(1) HCl (2) HF
(3) H_2O (4) NH_3

94. Which one of the following hydrogen halides has the lowest boiling point?
(1) HF (2) HCl
(3) HBr (4) HI

95. Out of the two compounds shown below, the vapour pressure of II at a particular temperature is expected to be

I. p-Hydroxy benzaldehyde ⇒


II. o-Hydroxy benzaldehyde ⇒


(1) Higher than that of I
(2) Lower than that of I
(3) Same as that of I
(4) Can be higher or lower depending upon the size of vessel

Bond Angle

96. The decreasing values of bond angles from NH_3 (106°) to SbH_3 (101°) down group-15 of the periodic table is due to
(1) Decreasing lp–bp repulsion
(2) Decreasing electronegativity
(3) Increasing bp–bp repulsion
(4) Decreasing p-orbital character in sp^3

97. In compound X all the bond angles around central atom are 109°28°. Which one of the following will be X?
(1) Chloromethane (2) Carbon tetrachloride
(3) Iodoform (4) Chloroform

98. In which of the following molecule, all the atoms lie in one plane?
(1) CH_4 (2) BF_3
(3) PF_5 (4) NH_3

99. The bond angles of NH_3, $NH_4^{\oplus}$ and $\overset{\ominus}{N}H_2$ are in the order:
(1) $NH_2^{\ominus} > NH_3 > \overset{\oplus}{N}H_4$ (2) $\overset{\oplus}{N}H_4 > NH_3 > \overset{\ominus}{N}H_2$
(3) $NH_3 > \overset{\ominus}{N}H_2 > \overset{\oplus}{N}H_4$ (4) $NH_3 > \overset{\oplus}{N}H_4 > \overset{\ominus}{N}H_2$

100. For AB_x type molecule, which statement(s) is(are) correct about bond angle (B–A–B)?
I. Bond angle ∝ EN of the central atom A.
II. Bond angle ∝ 1/EN of the central atom A.
III. Bond angle ∝ Size of central atom.
IV. Bond angle ∝ 1/Size of central atom.
(1) I, II, III (2) II, IV
(3) I, IV (4) II, III

101. For AB_x type molecule, which statement(s) is (are) correct about bond angle (B-A-B)
I. Bond angle ∝ 1 / EN of atom B.
II. Bond angle ∝ EN of atom B.
III. Molecules or ions without non-bonding electrons on central atom and having regular geometry, the change in EN of A or B has no effect on the bond angle.
IV. The bond angle in compounds having sp, sp^2 and sp^3 hybridisation on central atom decreases as follows:
$sp > sp^2 > sp^3$.
(1) I, IV (2) II, IV
(3) I, II, III (4) I, II, IV

102. Decreasing order of bond angle of (I) NO_2, (II) $NO_2^{\oplus}$ and (III) $NO_2^{\ominus}$ is
(1) I > II > III (2) II > I > III
(3) III > II > I (4) III > I > II

103. Decreasing order of bond angle of (I) NF_3, (II) PH_3 (III) AsF_3 is
(1) I > II > III (2) I > III > II
(3) II > I > III (4) III > II >I

104. Which statement is correct about bond angle of NCl_3, NF_3 and NH_3.
I. Bond angle of $NCl_3 > NF_3$.
II. Bond angle of $NCl_3 < NF_3$.
III. Bond angle of $NH_3 > NF_3$.
IV. Bond angle of $NH_3 < NF_3$.
(1) I, II (2) I, III
(3) I, II, III (4) I, II, IV

105. Bond order of SO_2 is
(1) 1.5 (2) 1.33
(3) 2.0 (4) 2.5

Resonance and Formal Charges

106. Which of the following conditions is not correct for resonating structures?
(1) The contributing structures must have the same number of unpaired electrons.
(2) The contributing structures should have similar energies.
(3) The contributing structures should be so written that unlike charges reside on atoms that are far apart.
(4) The positive charge should be present on the electropositive element and the negative charge on the electronegative element.

107. Resonance structures can be written for
(1) O_3 (2) NH_3
(3) CH_4 (4) H_2O

108. The bond length of C = O bond in CO is 1.20 Å and in CO_2 it is 1.34 Å. Then C = O bond length in CO_3^{2-} will be
(1) 1.50Å (2) 1.34Å
(3) 1.29Å (4) 0.95Å

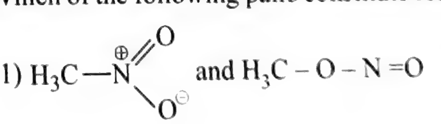
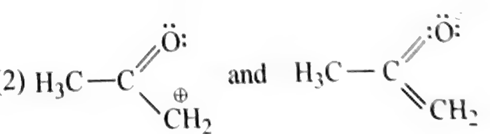
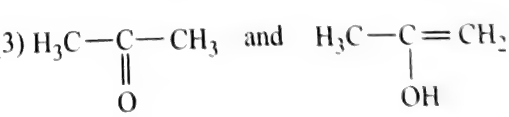
109. Maximum number of H-bonds that can be formed by a water molecule is
(1) 2 (2) 3
(3) 4 (4) 6

110. Which of the following resonating structures is not correct for CO_2?
(1) :Ö=C=Ö: (2) $:\ddot{O}^{\ominus}$—C≡$O^{\oplus}$:
(3) $^{\oplus}\ddot{O}$—C≡$\ddot{O}^{\ominus}$ (4) $:O^{\oplus}$≡C—$\ddot{O}^{\ominus}$:

111. In PO_4^{3-} the formal charge on each O-atom and P–O bond order respectively are
(1) –0.75, 1.0 (2) –0.75, 1.25
(3) –0.75, 0.6 (4) –3, 1.25

112. The formal charge of the O-atoms in the ion [: N̈ = Ö :] is
(1) 0 (2) + 1
(3) –1 (4) –2

113. Which of the following statements regarding the concept of resonance **is** wrong?
(1) The different resonating structures of a molecule have fixed arrangement of atomic nuclei.
(2) The different resonating structures differ in the arrangement of electrons.
(3) None of the individual resonating structures explains the various characteristics of the molecule.
(4) The hybrid structures have equal contribution from all the resonating structures.

114. Which of the following pairs constitute resonance structure?
(1) 
(2) 
(3) 
(4) $H_3C - CH = CH - CH_3$ and $H_3C - CH_2 - CH = CH_2$

115. Which of the following statement about resonance energy is wrong?
(1) The difference in energy of the resonance hybrid and the most stable contributing structures (having least energy) is called resonance energy.
(2) The difference in energy of the resonance hybrid and the least stable contributing structures (having highest energy) is called resonance energy.

(3) The difference in the experimental and calculated enthalpies (bond enthalpy, formation or combustion or hydrogenation) is called resonance energy.

(4) Resonance energy is the amount of energy by which the compound is stable.

Molecular Orbital Theory (MOT)

116. During the formation of a molecular orbital from atomic orbitals, the electron density is
(1) Minimum in the nodal plane
(2) Maximum in the nodal plane
(3) Zero in the nodal plane
(4) Zero on the surface of the lobe

117. Which of the following have been arranged in increasing bond order as well as bond dissociation energy?
(1) $O_2^{-2} < O_2^{\ominus} < O_2^{\oplus} < O_2$ (2) $O_2^{-2} < O_2^{\ominus} < O_2 < O_2^{\oplus}$
(3) $O_2 < O_2^{\oplus} < O_2^{2-} < O_2^{\ominus}$ (4) $O_2^{\oplus} < O_2^{2-} < O_2^{\ominus} < O_2$

118. In forming (i) $N_2 \rightarrow N_2^{\oplus}$ and (ii) $O_2 \rightarrow O_2^{\oplus}$; the electrons respectively are removed from:
(1) (π^*2p_y or π^*2p_x) and (π^*2p_y or π^*2p_x)
(2) (π $2p_y$ or π $2p_x$) and ($\pi 2p_y$ or $\pi 2p_x$)
(3) ($\pi 2p_y$ or $\pi 2p_x$) and (π^*2p_y or π^*2p_x)
(4) (π^*2p_y or π^*2p_x) and ($\pi 2p_y$ or $\pi 2p_x$)

119. The species that does not show paramagnetism is
(1) O_2 (2) $O_2^{\oplus}$
(3) O_2^{2-} (4) $H_2^{\oplus}$

120. Which of the following cannot exist on the basics of MO theory ?
(1) $H_2^{\oplus}$ (2) $He_2^{\oplus}$
(3) He_2 (4) O_2

121. Which one is paramagnetic and has a bond order of 0.5?
(1) $H_2^{\oplus}$ (2) F_2
(3) $N_2^{\oplus}$ (4) O_2

122. The bond energies NO, $NO^{\oplus}$ and $NO^{\ominus}$ follow the order:
(1) $NO^{\oplus} > NO > NO^{\ominus}$ (2) $NO > NO^{\oplus} > NO^{\ominus}$
(3) $NO^{\ominus} > NO > NO^{\oplus}$ (4) $NO^{\oplus} > NO^{\ominus} > NO$

123. In the MO diagram for $O_2^{\ominus}$ ion, the highest occupied orbital is
(1) π MO orbital (2) σ MO orbital
(3) π^* MO orbital (4) σ MO orbital

124. Which of the following is not diamagnetic?
(1) O_2^{2-} (2) Li_2
(3) $N_2^{\oplus}$ (4) C_2

125. The bond order of CO and NO is
(1) 3 and 2 (2) 3 and 2.5
(3) 3 and 1.3 (4) 3 and 3.5

126. Combination of two AO's lead to the formation of
(1) 2 MO's (2) 1 MO
(3) 3 MO's (4) 4 MO's

127. The possible molecular orbital formed when two d-orbitals overlap is
(1) π (2) π^*
(3) σ^* (4) δ^*

128. Which of the following species exhibits the diamagnetic behaviour?
(1) NO (2) O_2^{2-}
(3) $O_2^{\oplus}$ (4) O_2

129. Which of the following species is paramagnetic?
(1) CO_2 (2) O_2^{2-}
(3) $CN^{\ominus}$ (4)NO

130. The bond order in NO is 2.5 while that in $NO^{\oplus}$ is 3. Which of the following statement is true for these two species?
(1) Bond length in NO > in $NO^{\oplus}$.
(2) Bond length in $NO^{\oplus}$ = in NO.
(3) Bond length in $NO^{\oplus}$ > in NO.
(4) Bond length is unpredictable.

131. When two AO's combine, energy of bonding MO is lowered by x while that of antibonding MO is raised by y. Then.
(1) $x = y$ (2) $x < y$
(3) $x > y$ (4) Can be any of these

132. In which of the following the double bond consists of the pi bonds.
(1) O_2 (2) Be_2
(3) C_2 (4) S_2

133. Which of the following MO's has two nodal planes?
(1) π $2p_y$ (2) σ $2s$
(3) π^* $2p_y$ (4) σ^* $2p_z$

134. Which of the following MO's has zero nodal planes?
(1) σ^* $1s$ (2) σ $1s$
(3) π $2p_x$ (4) π^* $2p_x$

135. Main axis of a diatomic molecule is Z. AO's p_x and p overlap to form which of the following orbitals?
(1) π-MO (2) σ-MO
(3) δ-MO (4) No bond will form

136. The paramagnetic property of the oxygen molecule is due to the presence of unpaired electrons present in:
(1) $(\pi^*\ 2p_y)^1$ and $(\pi^*\ 2p_x)$ (2) $(\sigma\ 2p_z)^1$ and $(\sigma^*\ 2p_z)^1$
(3) $(\pi\ 2p_x)^1$ and $(\pi^*\ 2p_y)^1$ (4) $(\sigma\ 2p_z)^1$and $(\pi\ 2p_y)^1$

137. Which one of the following combination is not allowed in the LCAO method for the formation of a molecular orbital (consider Z-axis as the molecular axis)?
(1) $s + p_x$ (2) $s + p_z$
(3) $p_x + p_x$ (4) $p_z + p_z$

138. The energy of σ $2s$ is greater than σ^* $1s$ orbital because
(1) σ $2s$ is bigger than σ^* $1s$ MO
(2) σ $2s$ is bonding whereas σ^* $1s$ is an ABMO
(3) σ $2s$ orbital has a greater value of n than σ^* $1s$ MO
(4) σ $2s$ orbital is formed only after σ^* $1s$

Miscellaneous

139. Which of the following statements is incorrect?
(1) NH_3 is more basic than PH_3.
(2) NH_3 has a higher boiling point than that of HF.

(3) N_2 is less reactive than P_4.

(4) The dipole moment of NH_3 is less than that of SO_2.

140. If one assumes linear structure instead of bent structure for water, then which one of the following properties cannot be explained?

(1) The formation of intermolecular hydrogen bond in water.

(2) The high boiling point of water.

(3) Solubility of polar compounds in water.

(4) Ability of water to form coordinate covalent bond.

141. Which is the wrong order for the stated property?

(1) $Ba > Sr > Mg$;	atomic radius
(2) $F > O > N$;	first ionisation enthalpy
(3) $Cl > F > I$;	electron affinity
(4) $O > Se > Te$;	electronegativity

142. Which is a correct statement about diborane structure ?

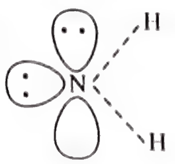
(1) All HBH bond angles are equal.

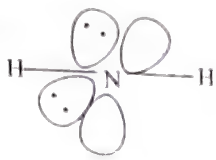
(2) All H–B bond lengths are equal.

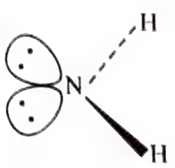
(3) It has two three-centre-2 electron bonds.

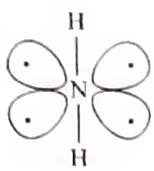
(4) All hydrogen and boron atoms are in one plane.

143. For $\overset{(-)}{N}H_2$, the best three-dimensional view is

(1) 

(2) 

(3) 

(4) 

144. The set representing the correct order of ionic radius is

(1) $Li^{\oplus} > Na^{\oplus} > Mg^{2+} > Be^{2+}$

(2) $Mg^{2+} > Be^{2+} > Li^{\oplus} > Na^{\oplus}$

(3) $Li^{\oplus} > Be^{2+} > Na^{\oplus} > Mg^{2+}$

(4) $Na^{\oplus} > Li^{\oplus} > Mg^{2+} > Be^{2+}$

145. Which of the following sets **does not** contain isoelectronic species?

(1) $PO_4^{3-}, SO_4^{2-}, ClO_4^{\ominus}$ (2) $SO_3^{2-}, CO_3^{2-}, NO_3^{\ominus}$

(3) $BO_3^{3-}, CO_3^{2-}, NO_3^{\ominus}$ (4) $CN^{\ominus}, N_2, C_2^{2-}$

146. The EN's of F, Cl, Br and I are 4.0, 3.0, 2.8 and 2.5 respectively. The hydrogen halide with a highest percentage of ionic character is

(1) HI (2) HBr

(3) HCl (4) HF

147. The C–C bond length is 1.54 Å. C=C bond length is 1.33 Å. What is the circumference of benzene ring? Bond length between single and double bonds = 1.4 Å.

(1) $(3 \times 1.54 + 3 \times 1.33)$ Å (2) $(4 \times 1.54 + 2 \times 1.33)$ Å

(3) (6×1.4) Å (4) $(4 \times 1.33 + 2 \times 1.54)$ Å

148. The correct order of the thermal stability of hydrogen halides (H – X) is

(1) $HI > HCl < HF > HBr$ (2) $HCl > HF > HBr > HI$

(3) $HF > HCl > HBr > HI$ (4) $HI > HBr > HCl > HF$

149. Which of the following statement is correct?

(1) The bond angle of NCl_3 is greater than that of NH_3

(2) The bond angle of PH_3 is greater than that of PF_3

(3) $ClO_3^{\ominus}$ and SO_3^{2-} are isostructural.

(4) It is not necessary that in Tbp structure the lone pairs always would occupy the equatorial positions.

150. The values of EN of atoms A and B are 1.80 and 4.0 respectively. The percentage of ionic character of A – B bond is

(1) 43% (2) 50%

(3) 55.3% (4) 65%

151. The statement true for azide ion ($N_3^{\ominus}$) is

(1) It has a non-linear structure

(2) It is called pseudo halogens

(3) The formal oxidation state of N in this anion is –1

(4) It is isoelectronic with NO_2

152. The decreasing (O – O) bond length order in the following is

(1) $O_2 > H_2O_2 > O_3$ (2) $H_2O_2 > O_3 > O_2$

(3) $O_3 > H_2O_2 > O_2$ (4) $O_3 > O_2 > H_2O_2$

153. Which of the following substance has the highest melting point?

(1) BaO (2) MgO

(3) KCl (4) NaCl

154. Which of the following statement is correct?

(1) $FeCl_2$ is more covalent than $FeCl_3$.

(2) $FeCl_3$ is more covalent than $FeCl_2$.

(3) Both $FeCl_2$ and $FeCl_3$ are equally covalent.

(4) $FeCl_2$ and $FeCl_3$ do not have any covalent character.

155. Which of the following bonds is the strongest?

(1) F – F (2) I – I

(3) Cl – Cl (4) O – O

156. The molecule having highest bond energy is

(1) N – N (2) F – F

(3) C – C (4) O – O

157. Which set is expected to show the smallest difference in IE_1?

(1) He, Ne, Ar (2) B, N, O

(3) Mg, $Mg^{\oplus}$, Mg^{+2} (4) Fe, Co, Ni

158. Which of the following statement is wrong?

(1) Multiple bonds are always shorter than the corresponding single bonds.

(2) The electron-deficient molecules act as Lewis acids.

(3) Every AB_5 molecule does in fact have square pyramidal structure.

(4) The canonical structure has no real existence

159. Which of the following is correct?

(1) According to VSEPR theory $SnCl_2$ is a linear molecule.

(2) The number of electrons present in the valence shell in SF_6 is 12.

(3) The rates of ionic compounds are very slow.
(4) The correct order of ability to form ionic compounds among $Na^{\oplus}$, Mg^{2+} and Al^{+3} is $Al^{+3} > Mg^{+2} > Na^{\oplus}$.

160. Lattice energy of $BeCO_3$ (I), $MgCO_3$ (II) and $CaCO_3$ (III) is in order:
(1) I < II < III (2) I > II > III
(3) I < III < II (4) II < I < III

161. Which of the following is a correct statement?
(1) Mobility of $H^{\oplus}$ ions in ice is greater as compared to liquid water.
(2) Mobility of $H^{\oplus}$ ions in ice is less as compared to liquid water.
(3) Mobility of $H^{\oplus}$ ions in ice is equal to that in liquid water.
(4) Cannot be predicted.

162. Which of the following is soluble in water:
(1) CS_2 (2) $CHCl_3$
(3) CCl_4 (4) CH_3OH

163. Which one among the following does not have the hydrogen bond?
(1) Liquid NH_3 (2) Liquid HCl
(3) Water (4) Phenol

164. The molecule having one unpaired electrons is
(1) O_2 (2) $CN^{\ominus}$
(3) NO (4) CO

165. The H-bond is strongest in:
(1) F – H .... O (2) S – H .... O
(3) O – H .... S (4) F – H .... F

166. Hydrogen bond is maximum in:
(1) Propanol (2) Propyl chloride
(3) Tripropylamine (4) Dipropyl ether

167. The maximum possible number of H-bonds a water molecule can form is
(1) 1 (2) 2
(3) 3 (4) 4

168. Number of paired electrons in O_2 molecule is
(1) 16 (2) 14
(3) 8 (4) 7

169. Among KO_2, $AlO_2^{\ominus}$, BaO_2 and $NO_2^{\oplus}$, unpaired electron is present in:
(1) KO_2 only (2) $NO_2^{\oplus}$ and BaO_2
(3) KO_2 and $AlO_2^{\ominus}$ (4) BaO_2 only

170. The correct order of decreasing C–O bond length of (I)CO, (II)CO_3^{2-} (III)CO_2 is
(1) I > III > II (3) I > II > III
(3) III > II > I (4) II > III > I

171. Which of the following statement is correct among the species $CN^{\ominus}$, CO and $NO^{\oplus}$:
(1) Isoelectronic and weak field ligands
(2) Isoelectronic with three bond order
(3) Bond order three and weak field ligands
(4) Bond order two and π-acceptor

172. Which of the following molecular species has unpaired electron(s)?
(1) O_2^{2-} (2) F_2
(3) N_2 (4) $O_2^{\ominus}$

173. Which of the following are isoelectronic and iso-structural?
$NO_3^{\ominus}$, CO_3^{2-}, $ClO_3^{\ominus}$, SO_3
(1) CO_3^{2-}, $ClO_3^{\ominus}$ (2) CO_3^{2-}, $NO_3^{\ominus}$
(3) SO_3, CO_3^{2-} (4) SO_3, $NO_3^{\ominus}$

174. According to MOT which of the following statement about magnetic character and bond order is correct regarding $O_2^{\oplus}$:
(1) Paramagnetic and BO > O_2
(2) Paramagnetic and BO < O_2
(3) Diamagnetic and BO > O_2
(4) Diamagnetic and BO < O_2

175. Which of the following compound is paramagnetic?
(1) K_2O_2 (2) O_3
(3) KO_2 (4) N_2O

176. The species having bond order different from that in CO is
(1) N_2 (2) $NO^{\ominus}$
(3) $NO^{\oplus}$ (4) $CN^{\ominus}$

177. In forming (i) $N_2 \rightarrow N_2^{\oplus}$ and (ii) $O_2 \rightarrow O_2^{\oplus}$, the electrons respectively removed from:
(1) (π^*2p_y or π^*2p_x) and ($\pi 2p_y$ or $\pi 2p_x$)
(2) (π^*2p_y or π^*2p_x) and (π^*2p_y or π^*2p_x)
(3) ($\pi 2p_y$ or $\pi 2p_x$) and ($\pi 2p_y$ or $\pi 2p_x$)
(4) ($\pi 2p_y$ or $\pi 2p_x$) and (π^*2p_y or π^*2p_x)

178. Using MOT, predict which of the following species has the shortest bond length?
(1) $O_2^{2\oplus}$ (2) $O_2^{\ominus}$
(3) O_2^{2-} (4) $O_2^{\oplus}$

179. Which of following have identical bond order? (One or more than one correct)
(1) $O_2^{\ominus}$ (2) $CN^{\ominus}$
(3) $NO^{\oplus}$ (4) $CN^{\oplus}$

180. If d_{xz} orbital of atom X and p_x orbital of atom Y from π bond along a particular molecular axis, then which bond will be formed along same molecular axis by combination of ($d_{xy} + d_{xy}$) orbitals of (X) and Y atom.
(1) δ-bond (2) σ-bond
(3) π-bond (4) Can't be predicted

181. Select correct statement.
(1) Order of σ-bond strength is:
$2p - 2p > 2s - 2p > 2s - 2s > 3s - 3s$
(2) d_{z^2} orbital can form π as well as δ-bond
(3) N_2CO has three structures, ONCN (Nitrocyl cyanide), ONNC (Nitrosyl isocyanide) and NOCN (isonitrosyl cyanide), amongst them ONCN has highest potential energy.
(4) Among $CH_3^{\oplus}$, B_2H_6, $NH_2^{\oplus}$ and AlF_3 only AlF_3 is hypovalent molecular species.

182. Which of the following overlap is correct (assuming Z-axis as internuclear axis)?
(I) $2p_x + 2p_x \longrightarrow \sigma$-bond
(II) $2s + 2p_y \longrightarrow \pi$-bond
(III) $3d_{xy} + 3d_{xy} \longrightarrow \pi$-bond
(IV) $3d_{xy} + 3d_{xy} \longrightarrow \pi$-bond
(V) $2p_y + 2p_y \longrightarrow \pi$-bond
(VI) $2p_z + 2p_z \longrightarrow \sigma$-bond
(1) I, II, III (2) IV, V, VI
(3) I, III, V (4) II, IV, VI

183. Which combination of orbitals will form π-bond, if inter nuclear axis is x-axis?
(1) $d_{xy} + d_{xy}$ (2) $d_{x^2-y^2} + d_{x^2-y^2}$
(3) $d_{yz} + d_{yz}$ (4) $p_x + p_x$

184. Which of the following orbital combination cannot form π-bond (all sideways overlapping)?
(1) $d_{x^2-y^2} + p_y$ (2) $d_{yz} + p_y$
(3) $d_{xy} + d_{xy}$ (4) $p_x + p_x$

185. Which of the following overlaps gives σ-bond along x-axis as internuclear axis?
(1) s and p_y (2) s and p_z
(3) $d_{x^2-y^2}$ and $d_{x^2-y^2}$ (4) p_z and p_z

186. Which of the following orbital combination can not form π-bond (all sideways overlapping)?
(1) $d_{yz} + p_y$ (2) $d_{x^2-y^2} + p_y$
(3) $d_{xy} + d_{xy}$ (4) $p_x + p_x$

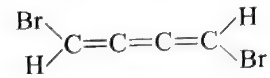
187. In which of the following species maximum atom can lie in same plane?
(1) $As^{\oplus}H_4$ (2) XeF_4
(3) PBr_5 (4) XeF_2O_2

188. Select the correct statement.
(1) In general, as the number of lone pair of e^-'s on central atom increases, value of bond angle from normal bond angle decreases.
(2) Geometry of $\overset{\ominus}{ICl_2}$ ion is bent shape with bond angle of about 90°.
(3) The hybridization of central atom changes when NH_3 vbforms $NH_2^{\ominus}$
(4) The hybridization of central atom does not change when H_3BO_3 reacts with $OH^{\ominus}$.

189. Select the incorrect statement.
(1) In C_3H_4 (allene) molecule, the planes containing the CH_2 groups are mutually perpendicular to permit the formation of two separate π-bonds.
(2) Nodal planes of π bonds in (CH_2=C=C=CH_2) located, two in molecular plane and one in a plane perpendicular to molecular plane which contains (C–C) σ-bond.
(3) Attraction between (I) ($Cl^{\ominus}$ and HCl molecule) and (II) ($Cl^{\ominus}$ and H_2O molecule), II have strongest attraction.
(4) Boiling point of $CH_3N_3 > HN_3$

190. Select the incorrect statement.
(1) Boiling point of $BI_3 >$ boiling point of BF_3
(2) Boiling point of $(CH_3)_2SO_4 >$ boiling point of H_2SO_4
(3) Boiling point of $B(OH)_3 >$ boiling point of $(CH_3)_3BO_3$
(4) Hybridization of central atom does not change during interaction of NH_3 with $H^{\oplus}$ ion.

191. Select the incorrect statement.
(1) Two different non axial d-orbitals having 'xz' nodal plane do not form π-bond
(2) Dipole moment (μ) of the given molecule is not zero



(3) In sp^3d^3 hybridization, d_{xy}, d_{yz} and d_{zx} d-orbitals are involved.
(4) I_2 molecules are held in the solid lattice by London forces

Multiple Correct Answers Type

Chemical Bonding

1. The type of bonding(s) present in NH_4Cl is(are):
(1) Ionic (2) Covalent
(3) Coordinate (4) Singlet

2. Which of the following statement(s) is(are) true?
(1) CuCl is more covalent than NaCl.
(2) HF is more polar than HBr.
(3) HF is less polar than HBr.
(4) Chemical bond formation takes place when forces of attraction overcome the forces of repulsion.

3. Which is(are) correct among the following?
(1) The radius of $Cl^{\ominus}$ ion is 1.56 Å, while that of $Na^{\oplus}$ ion is 0.95 Å.
(2) The radius of Cl atom is 0.99, while that of Na atom is 1.54.
(3) The radius of Cl atom is 0.95, while that of $Cl^{\ominus}$ ion is 0.81.
(4) The radius of Na atom is 0.95, while that of $Na^{\oplus}$ ion is 1.54.

4. Which of the following is(are) correct?
(1) A double bond is shorter than a single bond.
(2) A σ-bond is weaker than a π-bond.
(3) A double bond is stronger than a single bond.
(4) A covalent bond is stronger than a hydrogen bond.

5. The non-metallic cation is present in
(1) CrO_2Cl_2 (2) VOCl
(3) OF_2 (4) PCl_3

6. Peroxo bond (– O – O –) is present in
(1) Na_2O_2 (2) CrO_5
(3) PbO_2 (4) SrO_2

7. Among the following, the electron-deficient compound is
(1) $BeCl_2$ (2) CCl_4
(3) PCl_5 (4) BCl_3

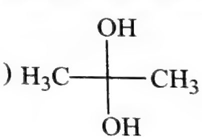
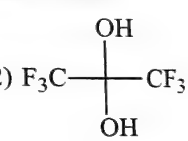
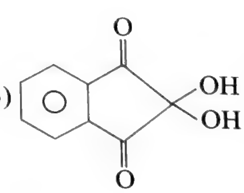
Dipole Moment

8. Which among the following molecules have minimum dipole moment?
   (1) CH_4 (2) CCl_4
   (3) CHI_3 (4) $CHCl_3$
9. Which of the following pairs of molecules have zero dipole moments for both members?
   (1) SiF_4 and CO_2 (2) SiF_4 and NO_2
   (3) O_2 and CO_2 (4) NO_2 and O_3
10. Which of the following statements are false?
   (1) Dipole–dipole interactions between molecules are greatest if the molecules possess only temporary dipole moments.
   (2) All compounds containing hydrogen atoms can participate in hydrogen bonding.
   (3) Dispersion forces exist between all atoms, molecules and ions.
   (4) The extent of ion-induced dipole interaction depends only on the charge of the ion.

Hybridisation

11. Which of the following are tetrahedral structures?
   (1) $[Ni(CN)_4]^{2-}$ (2) $[Ni(CO)_4]$
   (3) $[NiCl_4]^{2-}$ (4) CrO_4^{2-}
12. Which among the following are isostructural?
   (1) XeO_2F_2, SF_4 (2) CO_2, $I_3^{\ominus}$
   (3) SO_3^{2-}, CO_3^{2-} (4) ClF_3, XeF_2
13. In which of the following molecules, all the atoms lie in one plane?
   (1) $\dot{N}H_3$ (2) PF_5
   (3) BF_3 (4) XeF_4
14. Which of the following have sp^3d hybridisation of the central atom?
   (1) XeF_4 (2) XeO_2F_2
   (3) $ClO_3^{\ominus}$ (4) BrF_3
15. Which are the species in which central atom undergoes sp^3 hybridisation?
   (1) SF_4 (2) SCl_2
   (3) SO_4^{2-} (4) H_2O
16. The pair of species having identical shapes for molecules of both species is?
   (1) BF_3, PCl_3 (2) XeF_2, CO_2
   (3) CF_4, SiF_4 (4) PF_5, IF_5
17. Which among the following is(are) having two lone pair of electrons on central atom?
   (1) CO_2 (2) ClF_3
   (3) SO_3^{2-} (4) XeF_4
18. The state of hybridisation of atoms in boric acid (H_3BO_3) is
   (1) sp^3 (2) sp^2
   (3) sp (4) None of these
19. Which of the following have sp^3d hybridisation?
   (1) SF_4 (2) $BrCl_3$
   (3) $XeOF_2$ (4) $H_3O^{\oplus}$
20. The hybridisation, number of lone pair of electron and shape of $I_3^{\ominus}$ is
   (1) sp^3d hybridisation
   (2) It has trigonal bipyramidal shape
   (3) It is linear
   (4) It has three lone pair of electrons
21. Which of following is(are) correct for B and N in $NH_3 \cdot BF_3$ adduct?
   (1) Both have sp^3 hybrid orbitals
   (2) Both have tetrahedral structures
   (3) N is sp^3 hybridised, while B is sp^2 hybridised
   (4) N in NH_3 is pyramidal, while B in BF_3 is planar
22. Which of the following is not square planar?
   (1) XeF_4 (2) XeF_2
   (3) $XeOF_4$ (4) CH_3Cl

Hydrogen Bonding

23. Which property is due to H-bonding?
   (1) High boiling point of water
   (2) Solubility of NH_3 in H_2O
   (3) Polar nature of halogen acid
   (4) High viscosity of H_3PO_4
24. Hydrogen bonds are present in
   (1) Ice (2) Solid CO_2
   (3) HF (4) Water
25. Which of the following gem-diol is stable?
   (1)  (2) 
   (3)  (4) None of these

Bond Angle

26. Bond angle in PH_3 is
   (1) Much less than NH_3 (2) Much less than PF_3
   (3) Slightly more than NH_3 (4) Much more than PF_3
27. Which statement(s) is(are) correct for bond angle?
   (1) $NH_3 > NF_3$ (2) $NF_3 > NCl_3$
   (3) $NO_2^{\oplus} > NO_2$ (4) $NO_3^{\ominus} > NO_2^{\ominus}$
28. Which statement(s) is(are) wrong for bond angle?
   (1) $CH \equiv CH > BF_3 > CH_4$ (2) $H_2O > NH_3$
   (3) $\overset{\oplus}{N}H_4 > NH_3 > PCl_5$ (4) $CO_2 > NH_3 > CH_4$
29. Bond angle in $I_3^{\ominus}$ is
   (1) More than ClO_2 (2) 180°
   (3) Less than ClO_2 (4) >109.5°

30. Which statement(s) is(are) correct for AB_x type molecule?
(1) If the EN of central atom decreases, the bond angle decreases.
(2) If the size of central atom increases, the bond angle decreases.
(3) If the EN of atom B decreases that bond angle increases.
(4) If the EN of atom B decreases, the bond angle decreases.

Molecular Orbital Theory (MOT)

31. Which of the following have identical bond orders?
(1) $O_2^{\ominus}$ (2) $CN^{\ominus}$
(3) $NO^{\oplus}$ (4) $CN^{\oplus}$

32. Which of the following diatomic molecule/ions have same bond order?
(1) O_2 (2) $CN^{\ominus}$
(3) N_2 (4) C_2

33. Which of the following species exhibit the paramagnetic behaviour?
(1) O_2 (2) $O_2^{\oplus}$
(3) NO (4) O_2^{2-}

34. Which of the following molecules has one unpaired electron in antibonding orbitals?
(1) CO (2) $O_2^{\ominus}$
(3) $O_2^{\oplus}$ (4) NO

35. Which of the following show paramagnetism?
(1) Na_2O (2) NO_2
(3) NO (4) KO_2

36. Which of the following is(are) correct statements?
(1) Probability of finding the electron in bonding MO is more than combining atomic orbitals.
(2) Bonding MO's are formed when same sign of orbitals overlap.
(3) d–d combination of atomic orbitals gives δ and δ* MO's.
(4) None of these.

37. Which of the following is(are) gerade (g) MO's?
(1) $\sigma\ 2s$ (2) $\sigma\ 2p_z$
(3) $\pi^*(2p_x)$ (4) σ^*2s

38. Which of the following is(are) ungerade (u) MO's?
(1) $\sigma^*(2p_z)$ (2) $\pi(2p_x)$
(3) $\pi(2p_y)$ (4) $\pi^*(2p_y)$

39. Which of the following MO's have one nodal plane?
(1) $\sigma\ 1s$ (2) σ^*1s
(3) $\sigma\ 2p_z$ (4) σ^*2p_z

40. Which of the following MO's have two nodal plane?
(1) $\sigma\ 2p_z$ (2) π^*2p_x
(3) π^*2p_y (4) σ^*2p_z

Miscellaneous

41. Select correct orders for corresponding property as indicated in bracket for the following:
(1) $NH_3 > BiH_3 > SbH_3 > AsH_3 > PH_3$ (Boiling point)
(2) $H_2O > H_2Te > H_2Se > H_2S$ (Boiling point)
(3) $NH_3 > PH_3 > AsH_3 > SbH_3$ (Basic character)
(4) $H_2O < H_2S < H_2Se < H_2Te$ (Acidic character)

42. Which one or more among the following involve(s) ($p\pi$–$d\pi$) bonding?
(1) $(SiH_3)_3N$: (2) $(CH_3)_3N$:
(3) $:\overset{\ominus}{C}Cl_3$ (4) $:\overset{\ominus}{C}F_3$

43. Paramagnetic pair(s) among the following is (are)
(1) $[BaO_2, NO_2]$ (2) $[KO_2, NO]$
(3) $[H_2O_2, NO]$ (4) $K_3[Fe(CN)_6]$, $CuCl_2$

44. Which of the following orders are correct for property indicated in brackets?
(1) $NH_3 > NF_3 > BF_3$ (dipole moment)
(2) $Cl > S > O > N$ (electron affinity)
(3) $Si > Mg > Al > Na$ (first ionisation enthalpy)
(4) $HClO_4 > HBrO_4 > HIO_4$ (pK_a values)

45. The first element of groups 13–16 differ from rest of the elements. This is due to
(1) Small size and high electronegativity
(2) Inability to expand the octet
(3) Ability to form strong $p\pi$–$p\pi$ multiple bonds
(4) Due to greater abundance

46. Select the correct statements:
(1) The heat of hydrogen of the dipositive earth metal ions increases with an increase in their ionic size.
(2) Hydration of alkali metal ions is less than that of group 2.
(3) Alkaline earth metal ions, because of their much larger charge-to-size ratio exert a much stronger electrostaic attraction on the oxygen of water molecule surrounding them.
(4) Melting point of sodium halides is as follows: $NaF > NaCl > NaBr > NaI$

47. White vitriol is not isomorphous with
(1) K_2SO_4 (2) $MgSO_4$
(3) $CaSO_4$ (4) H_2SO_4

48. The stability of ions of Ge, Sn and Pb will be in the order
(1) $Ge^{2+} < Sn^{2+} < Pb^{2+}$ (2) $Pb^{2+} > Pb^{4+}$
(3) $Sn^{4+} > Pb^{2+}$ (4) $Ge^{4+} < Sn^{4+} < Pb^{4+}$

49. Select the correct statement(s).
(1) NF_3 is weaker base than NH_3.
(2) $NO^{\oplus}$ is more stable than O_2.
(3) $AlCl_3$ has higher melting point than AlF_3.
(4) $SbCl_3$ is more covalent than $SbCl_5$.

50. Which of the following are true?
(1) SH_6 and $BiCl_5$ do not exist.
(2) There are two $p\pi$–$d\pi$ bonds in SO_3.
(3) SeF_4 and CH_4 are tetrahedral ion.
(4) $I_3^{\ominus}$ is a linear molecule with sp^3d hybridisation

51. Select the correct statements.

(1) In $BF_2.NH_2$ molecule, FBF bond angle < 120° and HNH bond angle > 109° 28′

(2) Dipole moment of R_3NO > dipole moment of R_3PO

(3) In $N(CH_3)_3$ and $(CH_3)_2O$, bond angle is found to be greater than expected but not due to back bonding

(4) $(2p\pi - 3d\pi)$, π-bond is stronger than $(2p\pi - 3p\pi)$, π-bond

52. Select the correct statement.

(1) σ-bond lies on the line joining the nuclei of bonded atom.

(2) Bond angle FCF in COF_2 is greater than ClCCl bond angle in $COCl_2$.

(3) $CCl_3^{\ominus}$ is more stable and weaker Lewis base than $\overset{\ominus}{C}F_3$

(4) Lewis basic character order is: $H_2O > SCl_2 > SeF_2$

53. Select correct statements.

(1) π-electron cloud lies on either side of the line joining the nuclei of bonded atoms

(2) Lewis basic character order is: $NH_3 > PH_3 > PF_3$

(3) Out of the following species, O_3, $\overset{\oplus}{Br}F_2$, $\overset{\oplus}{B}H_4$ and $\overset{\oplus}{N}H_4$, dative bond is not present in $\overset{\oplus}{Br}F_2$.

(4) The combination of atomic orbitals $(d_{yz} + d_{yz})$ form π-bond having plane in yz plane

54. Select the correct statements.

(1) σ-bond has primary effect to decide direction of covalent bond, whereas π-bond has no primary effect in direction of bond.

(2) There is a change in the hybridization of P atom on solidification of PCl_5 vapour.

(3) There is a change in the hybridization of B atom when B_2H_6 is dissolved in THF.

(4) There is no change in the hybridization of Si atom when SiF_4 vapour is passed through liquid HF.

55. Select the incorrect statements.

(1) Van der Waals forces are responsible for formation of molecular crystals.

(2) In diamond, Vander Waals forces act between the carbon layers.

(3) When $Al(OH)_3$ ppt. is dissolved in NaOH, there is no change in the hybridization of Al-atom

(4) B_2 and C_2 both are paramagnetic

56. Select correct statements.

(1) For $NO \longrightarrow NO^{\oplus}$ bond length decrease whereas for $CO \longrightarrow CO^{\oplus}$ bond length increase

(2) In B_2H_6 and Al_2Cl_6 vacant hybrid orbital take part in bonding

(3) Compound $NO[BF_4]$ is diamagnetic

(4) Lewis basic character order is: $N(CH_3)_3 > NH_3 > NF_3$

57. Select the correct statements about the structure of H_2CSF_4.

(1) Two (C–H) bonds are in the same plane of equatorial S-F bonds.

(2) Two (C-H) bonds are in the same plane of axial S-F bonds.

(3) Equatorial S-F plane is perpendicular to the nodal plane of π-bond.

(4) Total four atoms are in the same plane.

58. Silane (SiH_4) is more reactive than CH_4 towards nucleophilic substitution reaction due to:

(1) Polarity of Si–H bond is opposite to that of C–H bond

(2) Large size of Si compared to C which facilitate the attack by nucleophile.

(3) Availability of vacant $3d$ orbitals in Si to form the reaction intermediate easily for nucleophilic attack.

(4) Si–H bond energy is higher than that of C–H bond.

59. Select correct statements about d_{z^2} orbital.

(1) It has zero nodal plane

(2) It is gerade atomic orbital

(3) Circular electron density is present in xy plane

(4) Opposite lobes of orbital have same sign of wave function (ψ)

60. Select the correct statements.

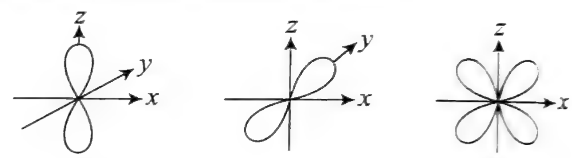
(1) Pure overlapping of two d_{xy} orbitals along x-axis results in the formation of π-bond.

(2) p_x orbital and d_{z^2} orbital do not form δ-bond.

(3) p_y orbital can not form π-bond by lateral overlap with d_{xy}, $d_{x^2-y^2}$ and p_z orbitals.

(4) $(2p\pi - 3d\pi)$ π-bond is stronger than $(2p\pi - 3p\pi)$

61. Consider the following three orbital:



(I) (II) (III)

Correct statement(s) regarding above orbitals is/are:

(1) If internuclear axis is 'x' then combination of (II) and (III) orbitals can form π-bond.

(2) Orbital (III) can form δ-bond with other orbital having same orientation of lobes.

(3) If internuclear axis is 'x' then combination of (I) and (II) orbitals can form π-bond.

(4) Orbitals (I) and (II) can never form any type of covalent bond.

62. Which of the following combination of orbitals does not form bond (if internuclear axis is x-axis)?

(1) $s + s$ (2) $d_{xy} + p_y$

(3) $s + p_z$ (4) $p_z + p_x$

63. Which of the following combination of bond pair $(b.p)$ and lone pair (lp) give same shape?

(I) $2b.p + 3\ lp$

(II) $3b.p + 2\ lp$

(III) $2b.p$ + zero lp

(IV) $2b.p + 1\ lp$

(V) $2b.p + 2\ lp$

(VI) $3b.p + 1\ lp$

(1) II and III (2) III and IV

(3) IV and V (4) I and III

64. Consider the following molecule:

$$\underset{1}{H_2C} = \underset{2}{C} = \underset{3}{C} = \underset{4}{C} = \underset{5}{CCl_2}$$

If hybridization of C_1 is sp^2 $(s + p_y + p_z)$ and hybridization of C_4 is sp $(s + p_z)$. Select correct statement(s) based on above information.

(1) Nodal plane of π-bond between C_1 and C_2 lies in yz-plane, formed by sideways overlap of p_y-orbitals.

(2) The orbitals involves in hybridization of C_5 atom are $s + p_x + p_z$.

(3) Nodal plane of π-bond between C_3 and C_4 lies in yz-plane, formed by sideways overlap of px-orbitals.

(4) Nodal plane of π-bond between C_2 and C_3 lies in xz-plane, formed by sideways overlap of p_y-orbitals.

Linked Comprehension Type

Paragraph 1

The shape of a molecule is determined by electron-pair repulsions in the valence shell. A *lp* occupies a larger space than a *bp* because it is not shared by two nuclei. Thus, the *lp–lp* repulsion is greater than the *lp–bp* repulsion, which in turn is greater than the *bp–bp* repulsion. The presence of *lp* causes distortion of bond angles; hence, a deviation from an ideal shape. The extent of distortion depends upon the orientation of the *lp*'s around the central atom. In a trigonal bipyramid, the *lp*'s occupy equatorial positions than the apical ones.

In AB_n type molecules, as the EN of A increases, the *bp*'s come closer and the repulsion between them increases. On the other hand, as EN of B increases, the *bp*'s get farther and repulsion decreases.

1. In which of the following molecules is the bond angle largest?
   (1) PF_3 (2) PCl_3
   (3) PBr_3 (4) PI_3

2. The shape of which of the following molecules will not be distored?
   (1) BrF_3 (2) ClF_3
   (3) XeF_4 (4) XeF_6

3. Which of the following statements is true?
   (1) F–N–F angle in NF_3 is greater than H–N–H angle in NH_3.
   (2) F–N–F angle in NF_3 is smaller than H–N–H angle in NH_3.
   (3) H–O–H angle in H_2O is greater than H–N–H angle in NH_3.
   (4) F–O–F angle in F_2O is greater than H–O–H angle in H_2O.

4. Which of the following species will have the lone pair effects cancelled?
   (1) $ICl_2^{\ominus}$ (2) ClF_3
   (3) PCl_3 (4) BrF_5

Paragraph 2

In MO energy diagrams for homonuclear diatomic molecules containing up to 14 or more than 14 e^-'s taken from both the atoms are filled from lower to higher energy MO's in accordance with Hund's rules.

The energy diagram of a heteronuclear diatomic molecule is similar. However, the energies of the AO's of the atom having higher atomic number being lower, the diagram will be unsymmetrical, but that will not make a difference in the electron count.

The bond order is half the difference in the number of electrons of the bonding (σ and π) and anti-bonding (σ and π) MO's For a bond to have been formed, the bond order should be greater than zero. The greater the bond order, the shorter is the bond distance and the greater is the bond dissociation energy. But if the bond order is same in the above two cases, then the bond distance will be greater and the bond dissociation energy smaller in the case which has more populated anti-bonding orbitals. The presence of unpaired electron(s) in a molecular orbital will make the system paramagnetic.

5. Which among the following will have a triple bond order?
   (1) CO (2) $CN^{\ominus}$
   (3) $NO^{\oplus}$ (4) All of these

6. Which of the following species is not expected to exist?
   (1) $He_2^{\oplus}$ (2) $H_2^{\ominus}$
   (3) Be_2 (4) $Be_2^{\ominus}$

7. Which of the following species is expected to be paramagnetic?
   (1) $NO^{\ominus}$ (2) $O_2^{\ominus}$
   (3) $O_2^{\oplus}$ (4) All of these

8. Which of the following orders is correct in respect of bond dissociation energy?
   (1) $N_2^{\oplus} > N_2^{\ominus}$ (2) $O_2 > O_2^{\ominus}$
   (3) $NO^{\oplus} > NO$ (4) All of these

Paragraph 3

Hydrogen bond is a weak bond formed between hydrogen atoms and highly electronegative elements. It is of two types — intermolecular and intramolecular. It is a weaker bond than ionic, covalent and metallic bonds.

9. Which is a correct statement?
   (1) Keto form of acetoacetic ester involves hydrogen bonding.
   (2) In water vapour, hydrogen bonding exists.
   (3) For first ionisation, maleic acid is a stronger acid than fumaric acid. This can be explained on the basis of concept of hydrogen bonding.
   (4) Boiling point of HCl is higher than that of HF.

10. In a suitable solvent such as benzene, benzoic acid associates and exists as a
   (1) dimer (2) trimer
   (3) tetramer (4) hexamer

11. The number of hydrogen bonds in $H_9O_4^{\oplus}$ species is
(1) 2 (2) 3
(3) 4 (4) 1

12. Which is a correct statement?
(1) Paranitrophenol is steam volatile but not orthonitrophenol.
(2) Ethyl alcohol is more viscous than glycerol.
(3) If a dry paper is torn, sound is heard due to breaking of hydrogen bonds one after another in a rhythmatic manner.
(4) In fermic salt, bonds present are covalent, metallic and hydrogen bond.

Paragraph 4

In an ionic bond, the cation tends to polarise the electron cloud of the anion by pulling electron density towards itself. This causes development of covalent character in the ionic bond because the electron density gets localised in-between the nuclei. The tendency of the cation to bring about the polarisation of the anion is expressed as its polarising power. The ability of ion to undergo polarisation is called its polarisability. The polarising power of a cation or an anion is decided on the basis of Fajans' rules as follows:

i. The smaller the cation, the higher is its polarising power.
ii. Cations with pseudo-noble gas configuration ($ns^2\,np^6\,nd^{10}$) have relatively high polarising power than those with noble gas configuration ($ns^2\,np^6$).
iii. The larger the size of the anion, the higher is its polarisability.

13. The ionic conductance of which of the following is the highest?
(1) $Li^{\oplus}_{(aq)}$ (2) $Na^{\oplus}_{(aq)}$
(3) $K^{\oplus}_{(aq)}$ (4) $Cs^{\oplus}_{(aq)}$

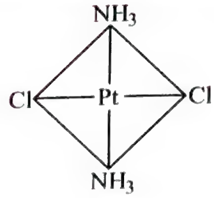
14. Among the following, which will have the lowest melting point and the highest solubility: LiCl, $BeCl_2$, BCl_3, CCl_4?
(1) CCl_4, LiCl (2) LiCl, CCl_4
(3) $BeCl_2$, BCl_3 (4) BCl_3, $BeCl_2$

15. Choose the correct order of polarisability for the following:
$I^{\ominus}$, $Br^{\ominus}$, $Cl^{\ominus}$, $F^{\ominus}$
(1) $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$ (2) $I^{\ominus} > Br^{\ominus} = Cl^{\ominus} > F^{\ominus}$
(3) $I^{\ominus} = Br^{\ominus} = Cl^{\ominus} > F^{\ominus}$ (4) $I^{\ominus} = Br^{\ominus} < Cl^{\ominus} = F^{\ominus}$

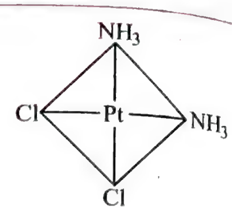
16. Arrange the following species in decreasing order of polarising powers: $Ag^{\oplus}$, $Tl^{\oplus}$, $Na^{\oplus}$.
(1) $Tl^{\oplus} > Ag^{\oplus} > Na^{\oplus}$ (2) $Tl^{\oplus} > Na^{\oplus} > Ag^{\oplus}$
(3) $Ag^{\oplus} > Tl^{\oplus} > Na^{\oplus}$ (4) $Na^{\oplus} > Tl^{\oplus} > Ag^{\oplus}$

Paragraph 5

The platinum–chlorine distance has been found to be 2.32 Å in several crystalline compounds. This value applies to both compounds A and B given here.



(A)



(B)

Based on the above structures, answer the following questions:

17. Cl—Cl distance in structure (A) is
(1) 2.32 Å (2) 4.64 Å
(3) 1.16 Å (4) 9.28 Å

18. Cl—Cl distance in structure (B) is
(1) 2.32 Å (2) 1.52 Å
(3) 2.15 Å (4) 3.28 Å

19. Structure A is
(1) *cis*-isomer (2) *trans*-isomer
(3) chiral isomer (4) none of these

20. Structure B is
(1) *cis*-isomer (2) nuclear isomer
(3) chiral isomer (4) co-ordinate isomer

21. The C—C single-bond distance is 1.54 Å. What is the distance between the terminal carbons in propane? Assume that the four bonds of any carbon atoms are pointed towards the corners of a regular tetrahedron.
(1) 3.08 Å (2) 1.54 Å
(3) 2.52 Å (4) 1.26 Å

Paragraph 6

The $HF_2^{\ominus}$ ion exists in the solid state and also in liquid HF but not in dilute aqueous solution.

22. $HF_2^{\ominus}$ exists in solid state and in liquid HF because $HF_2^{\ominus}$ ions are held together by
(1) hydrogen bonding (2) van der Waals force
(3) London force (4) all of these

23. In aqueous solution
(1) HF forms $H_2F^{\oplus}$ and $\overset{\ominus}{O}H$, H_2O being a stronger acid than HF
$H_2O + HF \rightleftharpoons H_2F^{\oplus} + \overset{\ominus}{O}H$
(2) HF forms $H_3O^{\oplus}$ and $F^{\ominus}$, H_2O being a weaker acid than HF
$H_2O + HF \rightleftharpoons H_3O^{\oplus} + F^{\ominus}$
(3) H-bonding between HF and H_2O is observed
(4) No change is observed

24. At 300 K and 1.00 atm, the density of HF is 3.17 g L^{-1}. We conclude that there is a
(1) dimer formation by H-bonding
(2) trimer formation by H-bonding
(3) tetramer formation by H-bonding
(4) ionisation formation $HF_2^{\ominus}$ and $H^{\oplus}$

25. Energy of H-bond is maximum in
(1) F—H---O (2) F—H---F
(3) O—H---O (4) O—H---F

26. Consider the following molecules:
A : Anti-pyridine-2-carboxaldoxime
B : syn pyridine-2-carboaxaldoxime
C : nickel-dimethyl glyoximate
D : *o*-nitrophenol
E : *p*-nitrophenol
F : *p*-salicylaldehyde
In which case chelate formation occurs?
(1) A, B (2) B, C
(3) C, F (4) C only

27. Intramolecular hydrogen bonding (in Q. 26) is observed in
(1) A, B, C, D (2) A, B, E, F
(3) B, C, D (4) A, C, D

Paragraph 7

Valence-bond theory is one of the two quantum mechanical approaches that explains bonding in molecules. In some cases, valence bond theory cannot satisfactorily account for observed properties of molecules.

28. Consider the following molecular geometries:
NO CO O_2
Select correct statement(s) about these: (More than one correct)
(1) NO is paramagnetic, CO and O_2 are diamagnetic
(2) NO and O_2 are paramagnetic, CO is diamagnetic
(3) Bond order is in order $O_2 < NO < CO$
(4) Number of unpaired electrons are

NO	1
CO	0
O_2	0

29. Valence-bond theory can explain molecular geometries:
(1) predicted by VSEPR model
(2) predicted by MO theory
(3) predicted by both (a) and (b)
(4) predicted by none of these

30. Bond order and magnetic behaviour shown by different species have been matched. Which is the incorrect matching?

Species	Bond order	Magnetic behaviour
(1) $CN^{\ominus}$ (14)	3.0	diamagnetic
(2) BN (12)	2.0	diamagnetic
(3) C_2 (12)	2.0	diamagnetic
(4) B_2 (10)	3.0	paramagnetic

31. MO electronic configuration of superoxide ion is
(1) KK^* $(\sigma 2s)^2$, $(\sigma^* 2s)^2$, $(\sigma 2p_z)^2$ $(\pi 2p_y)^2$ $(\pi 2p_x)^2$ $(\pi^* 2p_y)^2$ $(\pi^* 2p_x)^1$
(2) KK^* $(\sigma 2s)^2$ $(\sigma * 2s)^2$ $(\sigma 2p_z)^2$ $(\pi 2p_x)^2$ $(\pi 2p_x)^2$ $(\pi * 2p_y)^2$ $(\pi * 2p_x)^2$
(3) KK^* $(\sigma 2s)^2$ $(\sigma * 2s)^2$ $(\sigma 2p_z)^2$ $(\pi 2p_y)^2$ $(\pi 2p_x)^2$ $(\pi * 2p_y)^2$
(4) none of the above

32. Which of the following statements is correct about $O_2, O_2^{\ominus}, O_2^{2-}$ species?
(1) KO_2 and K_2O_2 are diamagnetic, while O_2 is paramagnetic
(2) KO_2 and O_2 are paramagnetic, while K_2O_2 is diamagnetic
(3) Bond length increase in the order: $O_2 < O_2^{\ominus} < O_2^{2-}$
(4) Bond enthalpy increase in the order: $O_2^{2-} < O_2^{\ominus} < O_2$

Paragraph 8

According to the molecular orbital theory, all atomic orbitals combine to form molecular orbital by LCAO (linear combination of atomic orbitals) method. When two atomic orbitals have additive (constructive) overlapping, they form bonding molecular orbitals (BMO) which have lower energy than atomic orbitals, whereas when atomic orbitals overlap subtractive, higher energy antibonding molecular orbitals (ABMO) are formed. Each MO occupies two electrons with opposite spin. Distribution of electrons in MO follows Aufbau principle as well as Hund's rule. MO theory can successfully explain the magnetic behaviour of molecules.

33. O_2^{2-} will have
(1) bond order equal to H_2 and diamagnetic
(2) bond order equal to H_2 but paramagnetic
(3) bond order equal to N_2 and diamagnetic
(4) bond order higher than O_2

34. Which of the following is/are not paramagnetic?
(1) NO (2) B_2
(3) CO (4) O_2

35. Bond strength increases when
(1) bond order increases
(2) bond length increases
(3) antibonding electrons increases
(4) bond angle increases

Paragraph 9

Most of the polyatomic molecules, except a few such as CO_2 and CS_2, are linear or angular with a bond angle generally somewhat greater than 90°. A bond angle is defined as the angle between the direction of two covalent bonds. Since the atoms in molecules are in constant motion with respect to each other, they are not expected to have a fixed value of bond angle. Repulsion between non-bonded atoms alone does not provide an adequate explanation. Hybridisation of bonding orbitals also plays a very important role in determining the value of bond angle. It has been observed that in hybridisation as the *s*-character of hybrid orbital increases, the bond angle increases.

36. In P_4 molecule phosphorous atoms are tetrahedrally arranged. The bond angle P–P–P in the molecule is
(1) 108° (2) 120°
(3) 60° (4) 180°

37. Which of the following have highest bond angle?
(1) H_2S (2) H_2Te
(3) H_2Se (4) All have same bond angle

38. Which of the following hybridisation may have more than one type of bond angle?
(1) sp^2 (2) sp^3
(3) sp^3d (4) sp^3d^2

Paragraph 10

MO's are formed by the overlap of AO's. Two AO's combine to form two MO's, called bonding molecular orbital (BMO) and antibonding molecular orbital (ABMO). Different AO's of one atom combine with these AO's of the second atom which have comparable energies and proper orientation. Further, if the overlapping is head on, the MO is called 'sigma' and if the overlap is lateral, the MO is called 'pi'. The MO's are filled with electrons following the same rules as followed for filling of atomic orbitals. However, the order of filling is not the same for all molecules or their ions. Bond order is one of the most important parameter to compare a number of their characteristics.

39. Which one of the following statements is correct?

(1) BMO is lowered by the same amount of energy by which ABMO is raised.

(2) BMO is lowered by a greater amount of energy than the amount by which ABMO is raised.

(3) BMO is lowered by less amount of energy than the amount by which ABMO is raised.

(4) Any one of the above is possible.

40. H_2, Li_2, B_2 each has bond order equal to 1. The order of their stability is

(1) $H_2 = Li_2 = B_2$ (2) $H_2 > Li_2 > B_2$

(3) $H_2 > B_2 > Li_2$ (4) $B_2 > Li_2 > H_2$

41. In which of the following pair, both the MO's are gerade or ungerade?

(1) $\sigma 2s$, $\pi 2p_x$ (2) $\sigma^* 2s$, $\pi^* 2p_x$

(3) $\sigma^* 2s$, $\pi 2p_x$ (4) $\pi 2p_x$, $\pi^* 2p_x$

42. Which one of the following has maximum number of nodal planes?

(1) $\sigma^* 1s$ (2) $\sigma^* 2p_z$

(3) $\pi 2p_x$ (4) $\pi^* 2p_y$

43. Which of the following pair is expected to have the same bond order?

(1) O_2, N_2 (2) $O_2^{\oplus}$, $N_2^{\ominus}$

(3) $O_2^{\ominus}$, $N_2^{\oplus}$ (4) $O_2^{\ominus}$, $N_2^{\ominus}$

Paragraph 11

Covalent bond is formed by overlapping of atomic orbitals of bonded atoms provided atomic orbitals must be half-filled and electrons should be in opposite spin. According to type of overlapping covalent bond can be classified as (a) σ-bond (b) π-bond (c) δ-bond.

44. The combination of orbital that cannot produce non-bonding molecular orbital is (if inter-nuclear axis is z-axis):

(1) $d_{xy} + d_{xy}$ (2) $s + d_{xz}$

(3) $p_y + d_{x^2-y^2}$ (4) $p_z + d_{yz}$

45. Which of the following set of orbitals does not produce nodal plane in xz-plane?

(1) $d_{xy} + d_{xy}$ (2) $p_y + d_{xy}$

(3) $d_{yz} + d_{yz}$ (4) None of these

46. In the molecule:

$$\underset{1}{Cl_2C} = \underset{2}{C} = \underset{3}{C} = \underset{4}{CCl_2}$$

If $Cl_2C_1 = C_2$ – lies in yz-plane, then incorrect statements is

(1) Nodal plane of π-bond between C_3 and C_4 lies in yz-plane, formed by sideways overlap of p_y-orbitals.

(2) Nodal plane of π-bond between C_2 and C_3 lies in xy-plane, formed by sideways overlap of p_z-orbitals.

(3) Nodal plane of π-bond between C_1 and C_2 lies in yz-plane, formed by sideways overlap of p_x-orbitals.

(4) Nodal plane of π-bond between C_2 and C_3 lies in xz-plane, formed by sideways overlap of p_y-orbitals.

Matrix Match Type

This section contains questions each with two Column I and II. Match the items in Column I with that in the Column II.

1.

	Column I		Column II
a.	sp^2	i.	XeF_4
b.	sp^3	ii.	BF_3
c.	sp^3d	iii.	$Br_3^{\ominus}$
d.	sp^3d^2	iv.	SO_4^{2-}

2.

	Column I (Compound)		Column II (Hybridisation of central atom)
a.	$[Ni(NH_3)_6]^{2+}$	i.	sp^3
b.	$[PtCl_4]^{2-}$	ii.	sp^3d^2
c.	$[Ni(CO)_4]$	iii.	dsp^3
d.	$[Co(ox)_3]^{3-}$	iv.	d^2sp^3

3.

	Column I		Column II
a.	$H_2O < H_2S < H_2Se < H_2Te$	i.	Bond angle
b.	$H_2O > H_2S > H_2Se > H_2Te$	ii.	Melting and boiling points
c.	$H_2O >> H_2S < H_2Se < H_2Te$	iii.	Acidic strength

4.

	Column I		Column II
a.	Methane molecules	i.	Covalency
b.	Sharing of electrons	ii.	Tetrahedral molecules
c.	H_2O	iii.	Pyramidal molecules
d.	NH_3	iv.	Polar molecule

5.

	Column I		Column II
a.	C_2H_2	i.	sp^2 hybridisation
b.	SO_2	ii.	sp^3d hybridisation
c.	SO_4^{2-}	iii.	sp^3 hybridisation
d.	$I_3^{\ominus}$	iv.	sp hybridisation

6.

	Column I		Column II
a.	SF_6	i.	sp^3d^3 hybridisation
b.	IF_7	ii.	sp^3d^2 hybridisation
c.	BeF_2	iii.	Zero dipole moment
d.	BF_3	iv.	Linear molecule

7.

	Column I		Column II
a.	σ bonding MO's and π antibonding MO's e.g., $\sigma 2s$ and $\pi^* 2p_y$	i.	Gerade
b.	σ^* antibonding MO's and π bonding MO's e.g., $\sigma^* 2s$, $\pi 2p_y$	ii.	Ungerade
c.	$\pi (2p_x)$	iii.	One nodal plane
d.	$\pi^* (2p_x)$	iv.	Two nodal plane

8.

	Column I		Column II
a.	C—H bond in ethyne	i.	sp–s overlap
b.	P—Cl bond in $POCl_3$	ii.	sp^3d–p overlap
c.	Br—Br bond in $Br_3^{\ominus}$	iii.	sp^3–p overlap
d.	C—C bond in ethane		sp^3–sp^3 overlap

9.

	Column I		Column II
a.	$ICl_2^{\ominus}$	i.	Participation of d-orbitals in hybridisation
b.	$NH_2^{\ominus}$	ii.	Hybrid orbitals contain 25% s-character
c.	$I_3^{\ominus}$	iii.	Central atom contains lp of electrons
d.	SO_4^{2-}	iv.	Non-linear geometry

10.

	Column I		Column II
a.	$H_2S_2O_5$	p.	O
b.	$H_2S_2O_3$	q.	+3
c.	$H_2S_4O_6$	r.	+5
d.	H_2SO_5	s.	+6
		t.	–2

11.

	Column I (Compounds)		Column II (Characteristics)
a.	H_3NBF_3	p.	Hypovalent compound
b.	H_4SiO_4	q.	Intermolecular H-bond
c.	H_2SeO_4	r.	Proton donor acid
d.	H_3BO_3	s.	Hypervalent compound
		t.	Back bond

12.

	Column I		Column II
a.	H_4SiO_4	p.	Bond angle of central atom increased due to combined effect of back bonding and steric factor.
b.	$B[N(CH_3)_2]_3$	q.	Anyone of t_{2g} d-orbital is involved in back bonding.
c.	$(SiH_3)_2O$	r.	Electron density on central atom decrease due to back bonding
d.	Single CCl_2	s.	Hybridisation of central atom does not change due to back bonding
		t.	Electron density on central atom increase due to back bonding.

13.

	Column I Characteristics		Column II Species
a.	The distribution of s-character in hybrid orbitals of central atom is not equal and all bond lengths (CA – X) are equivalent	p.	$\overset{\oplus}{P}Cl_4$
b.	The distribution of s-character in hybrid orbitals of central atom is equal and all bond lengths (CA – X) are equivalent	q.	NH_3
c.	The distribution of s-character in hybrid orbitals of central atom is not equal and bond angle (X – CA – X) is greater than 109° 28′	r.	R_2O
d.	The distribution of s-character in hybrid orbitals of central atom is equal and bond angle (X – CA – X) is either equal or less than 109° 28′	s.	XeO_6^{4-}
		t.	H_2O

14.

	Column I (Reactions)		Column II (Characteristics of Final Products)
a.	$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4$ (white ppt)	p.	$(p\pi - d\pi)$ bonds

b.	$MgSO_4 \xrightarrow[900°C]{\Delta} MgO + SO_2 + \frac{1}{2}O_2$	q.	Planar covalent species is formed
c.	$H_3BO_3 + OH^{\ominus}$	r.	Lone pair(s) is/are present at central atom.
d.	Self ionization of I_2	s.	*d*-orbitals involved in hybridisation of central atom of either of product
		t.	*d*-orbitals not involved in hybridisation of central atom of either of product

15.

Column I (Type of Bond Formed)		Column II Combining orbitals (Inter-nuclear axis)	
a.	σ-bond	p.	$d_{yz} + p_y, (z)$
b.	π-bond	q.	$s + p_x, (y)$
c.	δ-bond	r.	$d_{yz} + d_{yz}\ (x)$
d.	Non-bonding	s.	$s + s\ (z)$
		t.	$s + d_{xy}, (y)$

16. Match the items given in Column I with that in Column II and III.

Column I Type of Intractions		Column II Strength		Column III Energy distance function	
a.	Ion dipole (Non-van der Waal's intractions)	i.	Moderately strong	p.	$\frac{1}{r^4}$
b.	Dipole-dipole (non-van der Waal's interactions)	ii.	very weak	q.	$\frac{1}{r^6}$
c.	Ion-induced dipole (Van der Waal's interaction)	iii.	strong	r.	$\frac{1}{r^3}$
d.	Dipole-induced dipole (Van der Waal's interaction)	iv.	very very weak	s.	$\frac{1}{r^2}$
e.	London dispersion forces or (Instantaneous dipole induced dipole interaction)	v.	weak		

17. Match the items given in Column I with that in Column II and III.

List-I		List -II		List-III	
a.	sp^3d	i.	d_{xy}, d_{yz}, d_{zx}	p.	Octahedral
b.	sp^3d^2	ii.	$d_{x^2-y^2}, d_{z^2}$	q.	Pentagonal bipyramidal
c.	sp^3d^3	iii.	d_{z^2}	r.	Trigonal bipyramidal

18. Match the items given in Column I with that in Column II and III.

Column I Molecule		Column II Hybridisation		Column III Number of ($p\pi$-$p\pi$) and ($p\pi$-$d\pi$) multiple bonds	
a.	SO_2	i.	sp^3d	p.	($p\pi$-$p\pi$) multiple bond = 1 ($p\pi$-$d\pi$) multiple bond =1
b.	SO_3	ii.	sp^3d^2	q.	($p\pi$-$p\pi$) multiple bond = zero ($p\pi$-$d\pi$) multiple bond =2
c.	XeO_2F_2	iii.	sp^2	r.	($p\pi$-$p\pi$) multiple bond = zero ($p\pi$-$d\pi$) multiple bond =1
d.	$XeOF_4$	iv.	sp^3	s.	($p\pi$-$p\pi$) multiple bond = zero ($p\pi$-$d\pi$) multiple bond =3
e.	XeO_3			t.	($p\pi$-$p\pi$) multiple bond = 1 ($p\pi$-$d\pi$) multiple bond = 2

For Q.19 to Q.21

Answer the questions given below by appropriately matching the information given in three column of the following table.

Column I Molecule/ ion		Column II Bond order		Column III Magnetic character (μ_{MM} value)	
a.	NO, & $CO^{\oplus}$	i.	3	p.	Paramagnetic $\mu_{MM} = \sqrt{3}$ BM
b.	$NO^{\oplus}$ & CO	ii.	2	q.	Two are diamagnetic and one is paramagnetic with $\mu_{MM} = \sqrt{8}$ BM
c.	BN, & $NO^{\ominus}$	iii.	2.5	r.	Diamagnetic

19. For CN molecule, correct combination is
(1) a–iii–p (2) b–i–r
(3) c–ii–p (4) b–ii–r

20. For $CN^{\ominus}$ ion, correct combination is
(1) a–iii–p (2) b–i–r
(3) c–ii–p (4) a–ii–p

21. For $CN^{\oplus}$ molecule, correct combination is
(1) a–iii–p (2) b–i–r
(3) c–iii–p (4) c–ii–q

Numerical Value Type

1. How many molecules among the following have zero dipole moment: NH_3, BF_3, NF_3, CCl_4?

2. Find the number of lone pairs of electrons present in OF_2.

3. How many of the following compounds violate octet rule?
i. BrF_5 ii. SF_6 iii. IF_7 iv. $XeOF_4$
v. ClF_2 vi. $PCl_4^{\oplus}$

4. The number of hypervalent species among the following: $ClO_4^{\ominus}$, BF_3, SO_4^{2-}, CO_3^{2-} is

5. The number of correct options is
i. $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$ (polarisability)
ii. $Li^{\oplus} > Na^{\oplus} > K^{\oplus} > Rb^{\oplus}$ (polarisation power)
iii. $H_2O > H_2S > H_2Se > H_2Te$ (order of b.pt.)
iv. $H_2^{\ominus} < H_2^{\oplus}$ (order of stability)

6. How many of the following compounds have sp^3 hybridisation?
i. SO_4^{2-} ii. SO_5^{2-} iii. PO_4^{3-} iv. PO_5^{3-}
v. $I_3^{\ominus}$ vi. CO_3^{2-} vii. CO_4^{2-}

7. How many of the following compounds have ($p\pi-d\pi$) multiple bonds?
i. SO_2 ii. SO_3 iii. $HSO_4^{\ominus}$ iv. SO_4^{2-}
v. SO_3^{2-} vi. $HSO_3^{\ominus}$

8. How many of the following oxides of nitrogen are paramagnetic?
i. N_2O ii. NO iii. N_2O_3 iv. NO_2
v. N_2O_4 vi. N_2O_5 vii. $NO_2^{\oplus}$ viii. $NO_2^{\ominus}$
ix. $NO_3^{\ominus}$

9. How many of the following species have bond order of 2.5?
i. $N_2^{\oplus}$ ii. $N_2^{\ominus}$ iii. $O_2^{\oplus}$ iv. $O_2^{\ominus}$
v. NO vi. CN

10. The number of correct options is
a. $P_2O_5 > ZnO > MgO > Na_2O_2$ (acidic strength)
b. $Tl_2O_3 > Tl_2O > Ga_2O_3 > Al_2O_3$ (basic strength)
c. $MnO > P_2O_5 > CrO_3 > Mn_2O_7$ (ionic character)
d. $H_2O > HF > NH_3$ (melting point)
e. $H_2O > HF > NH_3$ (boiling point)

11. Out of the following orbitals, the total number of orbitals which can overlap. Colaterally (if internucleus axis is z).
(1) s (2) p_x (3) p_y (4) p_z
(5) d_{xy} (6) d_{yz} (7) d_{zx} (8) $d_{x^2-y^2}$
(9) d_{z^2}

12. Out of the following orbitals, the total number of orbital(s) having odd number of nodal plane are:
(1) $3s$ (2) $2p_x$ (3) $4s$ (4) $4p_z$
(5) $3p_y$ (6) $3d_{x^2-y^2}$ (7) $4d_{z^2}$ (8) $4d_{xy}$

13. How many possible < FSeF bond angle are present in SeF_4 molecule.

Archives

JEE MAIN

Single Correct Answer Type

1. Among the following the maximum covalent character is shown by the compound:
(1) $FeCl_2$ (2) $SnCl_2$
(3) $AlCl_3$ (4) $MgCl_2$ **(AIEEE 2011)**

2. The hybridization of orbitals of N atom in NO_3^-, NO_2^+, and NH_4^+ are respectively:
(1) sp, sp^2, sp^3 (2) sp^2, sp, sp^3
(3) sp, sp^3, sp^2 (4) sp^2, sp^3, sp
(AIEEE 2011)

3. The structure of IF_7 is
(1) square pyramidal (2) trigonal bipyramidal
(3) octahedral (4) pentagonal bipyramidal
(AIEEE 2011)

4. Which of the following has maximum number of lone pairs associated with Xe?
(1) XeO_3 (2) XeF_4
(3) XeF_6 (4) XeF_2 **(AIEEE 2011)**

5. Molecule having the smallest bond angle is
(1) NCl_3 (2) $AsCl_3$
(3) $SbCl_3$ (4) PCl_3 **(AIEEE 2012)**

6. In which of the following pairs, the two species are not isostructural?

(1) CO_3^{2-} and NO_3^- (2) PCl_4^+ and $SiCl_4$
(3) PF_5 and BrF_5 (4) AlF_6^{3-} and SF_6

(AIEEE 2012)

7. In which of the following pairs of molecules/ions both the species are not likely to exist?
(1) H_2^+, He_2^{2-} (2) H_2^-, He_2^{2-}
(3) H_2^+, He_2 (4) H_2^-, He_2^{2+}

(JEE Main 2013)

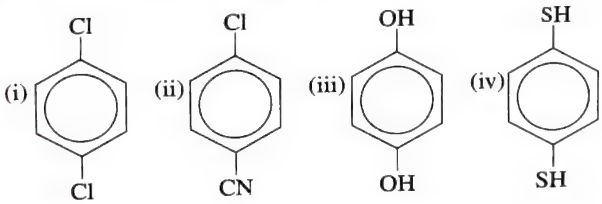
8. Stability of the species Li_2, Li_2^-, and Li_2^+ increases in the order of
(1) $Li_2 < Li_2^+ < Li_2^-$ (2) $Li_2^- < Li_2^+ < Li_2$
(3) $Li_2 < Li_2^- < Li_2^+$ (4) $Li_2^- < Li_2 < Li_2^+$

(JEE Main 2013)

9. The correct statement for the molecule CsI_3 is
(1) It is covalent molecule
(2) It contains Cs^+ and I_3^-
(3) It contains Cs^{3+} and I^- ions
(4) It contains Cs^+, I^- and lattice I_2 molecule

(JEE Main 2014)

10. For which of the following molecule significant $\mu \neq 0$?



(1) Only (i) (2) (i) and (ii)
(3) Only (iii) (4) (iii) and (iv)

(JEE Main 2014)

11. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is:
(1) ion–ion interaction (2) ion–dipole interaction
(3) London force (4) hydrogen bond

(JEE Main 2015)

12. Which one has the highest boiling point?
(1) He (2) Ne
(3) Kr (4) Xe **(JEE Main 2015)**

13. Which one of the following statements about water is FALSE?
(1) Ice formed by heavy water sinks in normal water.
(2) Water is oxidized to oxygen during photosynthesis.
(3) Water can act both as an acid and as a base.
(4) There is extensive intramolecular hydrogen bonding in the condensed phase. **(JEE Main 2016)**

14. The species in which the N atom is in a state of *sp* hybridization is:
(1) NO_2 (2) NO_2^+
(3) NO_2^- (4) NO_3^- **(JEE Main 2016)**

15. Which of the following species is not paramagnetic?
(1) NO (2) CO
(3) O_2 (4) B_2 **(JEE Main 2017)**

16. Total number of lone pair of electrons in I_3^- ion is
(1) 6 (2) 9
(3) 12 (4) 3 **(JEE Main 2018)**

17. According to molecular orbital theory, which of the following will not be a viable molecule?
(1) He_2^+ (2) H_2^-
(3) H_2^{2-} (4) He_2^{2+} **(JEE Main 2018)**

18. Which of the following compounds contain(s) no covalent bond(s)?
KCl, PH_3, O_2, B_2H_6, H_2SO_4
(1) KCl, H_2SO_4 (2) KCl
(3) KCl, B_2H_6 (4) KCl, B_2H_6, PH_3

(JEE Main 2018)

JEE ADVANCED

Single Correct Answer Type

1. The species having pyramidal shape is
(1) SO_3 (2) BrF_3
(3) SiO_3^{2-} (4) OSF_2

(IIT-JEE 2010)

2. Assuming 2*s*-2*p* mixing is NOT operative, the paramagnetic species among the following is
(1) Be_2 (2) B_2
(3) C_2 (4) N_2

(JEE Advanced 2014)

3. The ionic radii (in Å) of N^{3-}, O^{2-} and $F^{\ominus}$ are respectively
(1) 1.36, 1.40 and 1.71 (2) 1.36, 1.71 and 1.40
(3) 1.71, 1.40 and 1.36 (4) 1.71, 1.36 and 1.40

(JEE Advanced 2015)

Multiple Correct Answers Type

1. The nitrogen oxide(s) cotaining N—N bond is/are
(1) N_2O (2) N_2O_3
(3) N_2O_4 (4) N_2O_5

(IIT-JEE 2010)

2. Hydrogen bonding plays a central role in the following phenomena:
(1) Ice floats in water
(2) Higher Lewis basicity of primary than tertiary amines in aqueous solutions
(3) Formic acid is more acidic than acetic acid
(4) Dimerisation of acetic acid in benzene

(JEE Advanced 2014)

3. When O_2 is adsorbed on a metallic surface, electron transfer occurs from the metal to O_2. The **TRUE** statement(s) regarding this adsorption is(are)
(1) O_2 is physisorbed
(2) heat is released
(3) occupancy of π^*_{2p} of O_2 is increased
(4) bond length of O_2 is increased

(JEE Advanced 2015)

4. The compound(s) with two lone pairs of electrons on the central atom is(are)

(1) BrF_5 (2) ClF_3
(3) XeF_4 (4) SF_4

(JEE Advanced 2016)

5. According to Molecular orbital theory,

(1) C_2^{2-} is expected to be diamagnetic
(2) O_2^{2+} is expected to have a long bond length than O_2
(3) N_2^+ and N_2^- have the same bond order
(4) He_2^+ has the same energy as two isolated He atoms

(JEE Advanced 2016)

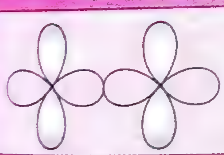
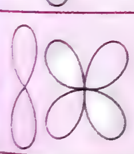
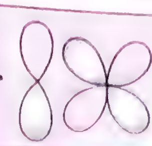
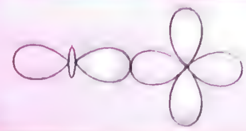
Matrix Match Type

1. Match each of the diatomic molecules in column I with its property/properties in column II.

Column I		Column II	
a.	O_2	p.	Paramagnetic
b.	$O_2^{\ominus}$	q.	Undergoes oxidation
c.	B_2	r.	Undergoes reduction
d.	N_2	s.	Bond order ≥ 2
		t.	Mixing of *s*- and *p*-orbitals

(IIT-JEE 2009)

2. Match the orbital overlap figure shown in List I with the description given in List II and select the correct answer using the code given below the lists.

List I	List II
p. 	1. *p–d* π-antibonding
q. 	2. *d–d* σ-bonding
r. 	3. *p–d* π-bonding
s. 	4. *d–d* σ-antibonding

Code:	p	q	r	s
(1)	2	1	3	4
(2)	4	3	1	2
(1)	2	3	1	4
(4)	4	1	3	2

(JEE Advanced 2014)

Numerical Value Type

1. Based on VSEPR theory, the number of 90° F — Br — F angles in a molecules of BrF_5 is ________ .

(IIT-JEE 2010)

2. Among the triatomic molecules/ions, $BeCl_2$, $N_3^{\ominus}$, N_2O, $NO_2^{\oplus}$, O_3, SCl_2, $ICl_2^{\ominus}$, $I_3^{\ominus}$ and XeF_2, the total number of linear molecule(s)/ion(s) where the hybridization of the central atom does not have contribution from the d-orbital(s) is **(JEE Advanced 2015)**

[Atomic number: S = 16, Cl = 17, I = 53 and Xe = 54]

3. Among H_2, $He_2^{\oplus}$, Li_2, Be_2, B_2, C_2, $N_2^{\ominus}$, and F_2, the number of diamagnetic species is

(Atomic numbers: H = 1, He = 2, Li = 3, Be = 4, B = 5, C = 6, N = 7, O = 8, F = 9) **(JEE Advanced 2017)**

4. The sum of the number of lone pairs of electrons on each central atom in the following species is

$[TeBr_6]^{2-}$, $[BrF_2]^+$, SNF_3, and $[XeF_3]^-$

(Atomic numbers: N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54)

(JEE Advanced 2017)

Answers Key

EXERCISES

Single Correct Answer Type

1. (2)	2. (3)	3. (2)	4. (1)	5. (2)
6. (2)	7. (3)	8. (1)	9. (1)	10. (4)
11. (4)	12. (1)	13. (4)	14. (1)	15. (2)
16. (3)	17. (1)	18. (4)	19. (3)	20. (4)
21. (1)	22. (4)	23. (3)	24. (3)	25. (4)
26. (2)	27. (4)	28. (4)	29. (4)	30. (1)
31. (3)	32. (1)	33. (1)	34. (3)	35. (1)
36. (3)	37. (1)	38. (2)	39. (2)	40. (4)
41. (4)	42. (1)	43. (1)	44. (2)	45. (3)
46. (1)	47. (3)	48. (3)	49. (2)	50. (2)
51. (2)	52. (1)	53. (2)	54. (1)	55. (2)
56. (2)	57. (4)	58. (4)	59. (2)	60. (2)
61. (4)	62. (1)	63. (2)	64. (3)	65. (1)
66. (3)	67. (2)	68. (4)	69. (1)	70. (1)
71. (1)	72. (3)	73. (2)	74. (1)	75. (4)
76. (2)	77. (3)	78. (1)	79. (1)	80. (2)
81. (3)	82. (2)	83. (1)	84. (2)	85. (1)

86. (2)	**87.** (4)	**88.** (2)	**89.** (4)	**90.** (1)
91. (1)	**92.** (2)	**93.** (2)	**94.** (2)	**95.** (1)
96. (2)	**97.** (2)	**98.** (2)	**99.** (2)	**100.** (3)
101. (4)	**102.** (2)	**103.** (1)	**104.** (2)	**105.** (2)
106. (3)	**107.** (1)	**108.** (3)	**109.** (3)	**110.** (3)
111. (2)	**112.** (1)	**113.** (4)	**114.** (2)	**115.** (2)
116. (3)	**117.** (2)	**118.** (3)	**119.** (3)	**120.** (3)
121. (1)	**122.** (1)	**123.** (3)	**124.** (3)	**125.** (2)
126. (1)	**127.** (4)	**128.** (2)	**129.** (4)	**130.** (1)
131. (2)	**132.** (3)	**133.** (3)	**134.** (2)	**135.** (4)
136. (1)	**137.** (1)	**138.** (3)	**139.** (2)	**140.** (3)
141. (2)	**142.** (3)	**143.** (3)	**144.** (4)	**145.** (2)
146. (4)	**147.** (3)	**148.** (3)	**149.** (3)	**150.** (4)
151. (3)	**152.** (2)	**153.** (2)	**154.** (2)	**155.** (3)
156. (3)	**157.** (4)	**158.** (3)	**159.** (2)	**160.** (2)
161. (1)	**162.** (4)	**163.** (2)	**164.** (3)	**165.** (4)
166. (1)	**167.** (4)	**168.** (2)	**169.** (1)	**170.** (4)
171. (2)	**172.** (4)	**173.** (2)	**174.** (1)	**175.** (3)
176. (2)	**177.** (4)	**178.** (1)	**179.** (2, 3)	**180.** (1)
181. (1)	**182.** (2)	**183.** (1)	**184.** (1)	**185.** (3)
186. (2)	**187.** (2)	**188.** (1)	**189.** (4)	**190.** (2)
191. (2)				

Multiple Correct Answers Type

1. (1, 2, 3)	**2.** (1, 2, 4)	**3.** (1, 2)
4. (1, 3, 4)	**5.** (3, 4)	**6.** (1, 2, 4)
7. (1, 4)	**8.** (1, 2)	**9.** (1, 3)
10. (1, 2, 4)	**11.** (2, 3, 4)	**12.** (1, 2)
13. (3, 4)	**14.** (2, 4)	**15.** (2, 3, 4)
16. (2, 3)	**17.** (2, 4)	**18.** (1, 2)
19. (1, 2, 3)	**20.** (1, 3, 4)	**21.** (1, 2)
22. (2, 3, 4)	**23.** (1, 2, 4)	**24.** (1, 3, 4)
25. (2, 3)	**26.** (1, 2)	**27.** (1, 3, 4)
28. (2, 4)	**29.** (1, 2)	**30.** (1, 2, 3)
31. (2, 3)	**32.** (2, 3)	**33.** (1, 2, 3)
34. (2, 3, 4)	**35.** (2, 3, 4)	**36.** (1, 2, 3)
37. (1, 2, 3)	**38.** (1, 2, 3)	**39.** (2, 4)
40. (1, 2, 3)	**41.** (2, 3, 4)	**42.** (1, 3)
43. (2, 4)	**44.** (1, 2, 3)	**45.** (1, 2, 3)
46. (2, 3, 4)	**47.** (1, 2, 3, 4)	**48.** (1, 2)
49. (1, 2)	**50.** (1, 2, 4)	**51.** (1, 2, 3, 4)
52. (1, 3, 4)	**53.** (1, 2, 3)	**54.** (1, 2)
55. (2, 3, 4)	**56.** (2, 3, 4)	**57.** (2, 3)
58. (1, 2, 3)	**59.** (1, 2, 3, 4)	**60.** (1, 2, 3, 4)
61. (2, 3, 4)	**62.** (3, 4)	**63.** (3, 4)
64. (2, 3, 4)		

Linked Comprehension Type

1. (4)	**2.** (3)	**3.** (2)	**4.** (1)	**5.** (4)
6. (3)	**7.** (4)	**8.** (4)	**9.** (3)	**10.** (1)
11. (2)	**12.** (3)	**13.** (4)	**14.** (1)	**15.** (1)
16. (3)	**17.** (2)	**18.** (4)	**19.** (2)	**20.** (1)
21. (3)	**22.** (1)	**23.** (2)	**24.** (3)	**25.** (2)
26. (4)	**27.** (4)	**28.** (2, 3)	**29.** (1)	**30.** (4)
31. (1)	**32.** (1)	**33.** (1)	**34.** (3)	**35.** (1)
36. (3)	**37.** (1)	**38.** (3)	**39.** (3)	**40.** (3)

41. (3)	**42.** (4)	**43.** (2)	**44.** (1)	**45.** (4)
46. (1)				

Matrix Match Type

S.No.	a	b	c	d	e
1.	ii	iv	iii	i	
2.	ii	iii	i	iv	
3.	iii	i	ii		
4.	ii	i	iv	iii	
5.	iv	i	iii	ii	
6.	ii	i, iii	iii, iv	iii	
7.	i	ii	iii	iv	
8.	i	iii	ii	iv	
9.	i, iii	ii, iii, iv	i, iii	ii, iv	
10.	q, r	s, t	p, r	s	
11.	p, q, t	q, r, t	q, r, s	p, q, t	
12.	q, s, t	s, t	p, q, r	p, s, t	
13.	q, r, t	p, s	r	p, s	
14.	p, t	p, q, r, t	t	q, s, r, t	
15.	s	p	r	q, t	
16.	iii, s	i, r	v, p	ii, q	iv, q
17.	iii, r	ii, p	i, q		
18.	iii, p	iii, t	i, q	ii, r	iv s

19. (1) **20.** (2) **21.** (4)

Numerical Value Type

1. (2)	**2.** (8)	**3.** (5)	**4.** (2)	**5.** (3)
6. (4)	**7.** (4)	**8.** (2)	**9.** (5)	**10.** (3)
11. (6)	**12.** (3)	**13.** (6)		

ARCHIVES

JEE Main

Single Correct Answer Type

1. (3)	**2.** (2)	**3.** (4)	**4.** (4)	**5.** (3)
6. (3)	**7.** (3)	**8.** (2)	**9.** (2)	**10.** (4)
11. (2)	**12.** (4)	**13.** (4)	**14.** (2)	**15.** (2)
16. (2)	**17.** (3)	**18.** (2)		

JEE Advanced

Single Correct Answer Type

1. (4) **2.** (3) **3.** (3)

Multiple Correct Answers Type

1. (1, 2, 3) **2.** (1, 2, 4) **3.** (1, 2, 3, 4)
4. (2, 3) **5.** (1, 3)

Matrix Match Type

1. (a → p, q, s; b → p, q; c → p, r; d → s)
2. (3)

Numerical Value Type

1. (8) **2.** (4) **3.** (6) **4.** (6)

3 Hydrogen, Water and Hydrogen Peroxide

OVERVIEW

1. Hydrogen was discovered by Henry Cavendish in 1766 by the action of acids and metals. It was named 'inflammable air'. Lavoisier named it hydrogen which means 'water producer'. The name 'hydrogen' has originated from the Greek words 'hydro' and 'genes' which mean 'water' and 'generator' respectively.
2. Hydrogen is the lightest element known. Its atom consists of a single proton and a single planetary electron. Its electronic configuration is $1s^1$. It is the only atom whose nucleus does not have any neutron.
3. Hydrogen is the most abundant element in the universe (70% of the universe's total mass). About half the mass of the sun and some other stars is made up of hydrogen. It is the third most abundant element on the surface of the earth. Hydrogen is the ninth element in order of abundance and forms 0.9% of earth's crust by weight. In the crustal rocks, it is the tenth in the order of abundance, ~ 0.15% by weight.
4. Naturally occurring hydrogen has three isotopes:
   a. Protium or ordinary hydrogen (^1_1H)
   b. Deuterium or heavy hydrogen (^2_1H or D)
   c. Tritium (^3_1H or T)

   Hydrogen is the only known element whose isotopes have the unique mass ratio of 1:2:3 (^1_1H: ^2_1H: ^3_1H), where protium (^1_1H) is the predominant form, deuterium (^2_1H) is present up to 0.156% in terrestrial hydrogen (mostly in the form of HD) and tritium (^3_1H) is radioactive. Tritium emits β-particles and its half life is 12–33 years.

   $$^3_1H \longrightarrow \underset{\beta\text{-particle}}{_{-1}e^0} + {}^3_2H$$
5. The three isotopes of hydrogen have the same chemical properties due to the same electronic configuration, but different physical properties due to different atomic masses.
6. Deuterium and tritium are used as tracers, bombarding projectiles especially in fusion reaction, i.e. in hydrogen bombs.
7. Atomic form of hydrogen exists only at high temperatures. Normal elemental hydrogen is the diatomic molecule called *dihydrogen*, H_2. But while referring to the isotopic mixture with the natural abundance for H and D, the name *disprotium* is preferred.
8. Hydrogen under very high pressure is expected to behave like a metal.
9. Heavy hydrogen or deuterium was separated from liquid hydrogen by fractional evaporation by Urey. For this great contribution, he was awarded the Nobel Prize in Chemistry in 1934.
10. The three main sources from which dihydrogen (ordinary hydrogen) may be prepared are (i) water, (ii) acids and (iii) alkalies.
    a. Group 1 and 2 elements react with water to produce H_2 gas. Since the reactions are vigorous, to minimise the rate of reactions, usually amalgams are used.
    b. Metals such as Zn, Fe, Mn, Co, Cr etc. decompose hot water or steam to form H_2.
    c. Steam reacts with hydrocarbons or coke at high temperature to produce H_2.

    $$C_nH_{2n+2} + nH_2O \xrightarrow[\text{Catalyst}]{1270\text{ K}} nCO + (2n+1)H_2$$

    $$C + H_2O \longrightarrow \underbrace{CO + H_2}_{\text{Water gas}}$$
    d. On electrolysis of water containing small amounts of acid or alkali, H_2 is produced at cathode.
    e. Ionic hydrides on hydrolysis evolve H_2.

    $$NaH + H_2O \longrightarrow NaOH + H_2\uparrow$$
    f. Metals which lie above hydrogen in the electrochemical series, e.g. Al, Mg, Zn, Fe etc. react with dil H_2SO_4 or dil HCl to produce H_2.

    $$Zn + \underset{\text{dil}}{H_2SO_4} \longrightarrow ZnSO_4 + H_2\uparrow$$
    g. Zn, Al, Sn, Si and Pb react with boiling NaOH or KOH to liberate H_2 gas.

    $$2Al + 2KOH + 2H_2O \longrightarrow 2KAlO_2 + 3H_2$$

    Uyeno's method is used for military purpose for rapid and pure production of H_2 when scrap Al reacts with caustic potash (KOH).
    h. In the laboratory, H_2 is produced by the action of H_2SO_4 on granular zinc.
11. Natural gas consists mainly of methane. Dihydrogen, H_2, is produced from natural gas either by partial oxidation or

by cracking.

$$CH_4 + H_2O \xrightarrow[\text{Ni–Cr}]{1200\text{ K}} CO + 3H_2$$

$$CH_4 \xrightarrow{\text{Cracking}} C + 2H_2$$

$$CO + H_2O \xrightarrow[Fe_2O_3]{750\text{ K}} CO_2 + H_2$$

CO_2 is removed by dissolving it in water under pressure of about 25–30 atm.

12. Dihydrogen is colourless, odourless and tasteless gas.
13. Dihydrogen has high heat of dissociation (436 kJ mol^{-1}). This property is used in atomic torch which generates temperature of ~ 4000 K and is ideal for welding of metals having high melting points.
14. The ordinary hydrogen at room temperature is a mixture of ortho- and para-form in the ratio 3:1. The proton (nuclei) of the ortho-hydrogen spins in the same direction, while that in the para-hydrogen spins in the opposite direction.
15. Certain metals, e.g. Pd, Pt, Fe, etc. can absorb large quantities of hydrogen. The absorbed hydrogen is called occluded hydrogen. This property can be used in the purification of hydrogen as only pure hydrogen is absorbed.
16. Dihydrogen is an inflammable or a combustible gas. But it does not help in burning. It burns with blue flame in oxygen atmosphere forming water.
17. Binary compounds of hydrogen with the elements in the periodic table are known as hydrides. Dihydrogen forms three types of hydrides
    a. Ionic/salt-like
    b. Covalent/molecular
    c. Metallic/interstitial

    Metallic hydrides are used for the ultrapurification of hydrogen and as hydrogen storage media.
18. Besides the three main categories of hydrides, certain hydrides are known as polymeric hydrides and complex hydrides.
19. Hydrogen has been considered as one of the alternate sources of energy. The advantages of using hydrogen as a fuel are as follows :
    a. It is environmentally clean.
    b. Heat of combustion of hydrogen per gram is higher than any other fuel.
    c. Our energy needs can be met by gaseous, liquid and solid hydrogen. However, cheaper modes of production of hydrogen, its storage and transportation are still a problem.
20. The most common and abundant compound of hydrogen is water. Water is essential to life, two-thirds of human body is water. Transformation of water from liquid to solid and to gaseous state is easy. It exists as a liquid under normal atmospheric condition. It exists as a solid below 0°C and as a gas above 100°C. The unique properties shown by water in liquid and solid state is due to extensive hydrogen bonding between water molecules. Water molecule forms four H-bonds. The density of water is maximum at 4°C.
21. Oxygen atom in H_2O is sp^3 hybridised with two lone pairs giving rise to bent or V-shaped structure, with a bond angle of 104.5°. Decrease in bond angle from 109.4° to 104.5° is due to *lp–lp* repulsion > *lp–bp* repulsion > *bp–bp* repulsion.
22. Ice has an open cage structure with a number of vacant spaces in the crystal lattice. Hence, the density of ice is less than water.
23. Water can be tested as follows:
    a. On addition of a drop of water to anhydrous copper sulphate, the colour changes from white to blue.
    $$\underset{\text{Anhydrous}}{CuSO_4} + 5H_2O \longrightarrow \underset{\text{Blue}}{CuSO_4{\cdot}5H_2O}$$
    b. On reaction with CaC_2, acetylene evolves which burns with bright flame.
    $$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{HC \equiv CH}$$
24. **Hard and soft water:** Depending upon its behaviour towards soap, water may be classified as hard or soft.
    a. Water which does not produce lather with soap readily is called hard water, e.g. sea water, river water etc.
    b. Water which produces lather with soap readily is called soft water, e.g. rain water, distilled water, demineralised water etc.
25. Hardness of water is due to the presence of calcium and magnesium salts of bicarbonates, carbonates and sulphates in water.
26. Hardness of water is of two types:
    a. **Temporary hardness:** Due to the presence of bicarbonates of calcium and magnesium, i.e. $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. This is also known as carbonate hardness.
    b. **Permanent hardness:** Due to the presence of soluble chlorides and sulphates of calcium and magnesium, i.e. $CaCl_2$, $CaSO_4$, $MgCl_2$ and $MgSO_4$. This is also known as non-carbonate hardness.
27. Removal of hardness of water:
    a. Temporary hardness can be easily removed by boiling or by adding slaked lime.
    b. Permanent hardness can be removed by water softeners such as (i) Ion-exchange resins, (ii) Calgon, (iii) Permutit, (iv) Washing soda etc.
28. Degree of hardness is defined as the number of parts of calcium and magnesium salts present in a million parts of water by mass. It is expressed in ppm.
29. Heavy water was discovered by Uery in 1932. One part of heavy water is present in 6000 parts of ordinary water (1 part in 6000). It is prepared by repeated electrolysis of water containing alkali. It is colourless, odourless and tasteless like ordinary water. Most of the physical constants of heavy water are higher than the corresponding value of ordinary water. Heavy water is used as moderator in nuclear reactors.

30. Deuterium peroxide, D_2O_2, is prepared by the action of D_2SO_4 (dissolved in H_2O) in BaO_2
$BaO_2 + D_2SO_4 \longrightarrow BaSO_4\downarrow + D_2O_2$
Deuterium chloride can be prepared by any of the following methods:
$2NaCl + D_2SO_4 \longrightarrow Na_2SO_4 + 2DCl$
$2AgCl + D_2 \longrightarrow 2Ag + 2DCl$
$SOCl_2 + 2D_2O \longrightarrow D_2SO_3 + 2DCl$

31. Hydrogen peroxide was discovered by Thenard. It is also known as oxygenated water.
$\underset{\text{dil}}{BaO_2 + H_2SO_4} \longrightarrow BaSO_4 + H_2O_2$

32. H_2O_2 cannot be stored in glass bottles as the rough surface of glass, alkali oxides present in it and exposure to light catalyses its decomposition.
$2H_2O_2 \longrightarrow 2H_2O + O_2$
Hence, H_2O_2 is normally stored in coloured paraffin wax-coated plastic or teflon bottles. Concentrated solution of H_2O_2 is stored in polythene bottles and are kept in refrigerators. Small amount of stabilisers such as orthophosphoric acid, acetanilide or sodium stannate are added.

33. H_2O_2 acts both as an oxidising and a reducing agent in the acidic as well as basic medium.
a. Oxidising agent:
i. In acidic medium: $H_2O_2 + 2H^{\oplus} + 2e^{\ominus} \longrightarrow 2H_2O$
ii. In basic medium: $H_2O_2 + 2e^{\ominus} \longrightarrow 2\overset{\ominus}{O}H$

b. Reducing agent:
i. In acidic medium: $H_2O_2 \longrightarrow 2H^{\oplus} + O_2 + 2e^{\ominus}$
ii. In basic medium: $H_2O_2 + 2\overset{\ominus}{O}H \longrightarrow 2H_2O + O_2 + 2e^{\ominus}$

34. H_2O_2 acts as a bleaching agent due to oxidation by nascent oxygen.
$H_2O_2 \longrightarrow H_2O + [O]$
H_2O_2 is used to bleach delicate article such as hair, silk, wood ivory etc.

35. H_2O_2 is used as antiseptic and germicide for washing wounds, teeth and ears under the trade name *perhydrol*.

36. H_2O_2 is used for restoring the colour of old paintings as it oxidises black PbS to white $PbSO_4$.

37. General formula of volume strength of H_2O_2:
a. 1.7% of $H_2O_2 \equiv 17\ g\ L^{-1}$ of $H_2O_2 \equiv 5.6$ L of O_2 at STP $\equiv 8$ g of O_2 at STP
b. Volume strength of $H_2O_2 \times$ Volume of H_2O_2 = Volume of O_2 at STP
c. 3% solution of H_2O_2 is marked as 10 volume H_2O_2
d. 30% solution of H_2O_2 is marked as 100 volume H_2O_2
e. Volume strength = 5.6 × Normality

$$= \frac{5.6 \times \text{Percentage strength}}{\text{EW of } H_2O_2} \times 10$$

f. Volume strength = 11.2 × Molarity

$$= \frac{11.2 \times \text{Percentage strength} \times 10}{\text{MW of } H_2O_2}$$

3.1 INTRODUCTION

Hydrogen was discovered by Henry Cavendish in 1766 in London, England, by the action of dilute H_2SO_4 on iron. The name 'hydrogen' was proposed by Lavoisier which means 'water producer', i.e. it produces water on burning with oxygen. It is originated from the Greek words 'hydro' and 'genes' which mean water and generator, respectively

3.2 ELECTRONIC CONFIGURATION

Hydrogen is the first element in the periodic table and also the lightest element known. It has the simplest atomic structure of all the elements and consists of one proton (in the nucleus) and one electron (in 1*s* orbital). Its atomic form exists only at high temperatures. In elemental form, it exists as a diatomic molecule, H_2, and is known as dihydrogen.

3.3 POSITION OF HYDROGEN IN THE PERIODIC TABLE

Period 1 of the periodic table comprises hydrogen (H) and helium (He). Hydrogen is quite reactive, while helium is inert. On the basis of the resemblance in the structure and properties of helium with the other noble gases, it is placed in group 18. However, a proper position for hydrogen could not be arranged in the periodic table due to the following reasons:

1. In some of its properties, hydrogen resembles group 1 elements, i.e. alkali metals and can be placed with them.
2. In some of its properties, hydrogen resembles group 17 elements, i.e. halogens and can be placed with them.
3. In some other properties, hydrogen differs from both group 1 (alkali metals) and group 17 elements.

3.3.1 COMPARISON WITH ALKALI METALS

3.3.1.1 Similarities Between Hydrogen and Alkali Metals

1. **Electronic configuration:** Both hydrogen and alkali metals (Li, Na, K, Rb, Cs and Fr) have one electron in their valence shell.
2. **Electropositive character:** Both exhibit an electropositive character and are monovalent, i.e. both have a tendency to lose the valence shell electron (less in case of H and more in case of alkali metals) to form unipositive ion ($M^{\oplus}$).

$$\underset{(1s^1)}{H} \longrightarrow \underset{(1s^0)}{H^{\oplus}} + e^{\ominus}$$

$$\underset{(1s^2\,2s^1)}{Li} \longrightarrow \underset{(1s^2)}{Li^{\oplus}} + e^{\ominus}$$

3. **Oxidation state:** Both show an oxidation state, +1 in their compounds.

$\overset{\oplus}{H}\overset{\ominus}{Cl}$ Hydrogen chloride

$\overset{\oplus}{Na}\overset{\ominus}{Cl}$ Sodium chloride

4. **Reducing character:** Both behave as strong reducing agents.
5. **Affinity for non-metals or electronegative elements:** Both have a strong affinity for non-metals as compared to metals, i.e. they react with electronegative elements. For example, on reaction with halogens, oxygen, sulphur, they form halides, oxides, sulphides, respectively.

Halides	HCl	NaCl
Oxides	H_2O	NaCl
Sulphides	H_2S	Na_2S

6. **Electrolysis:** On electrolysis of an aqueous solution of hydrogen halides (e.g. HCl) or oxide (H_2O), dihydrogen (H_2) is liberated at the cathode.

$$HCl_{(aq)} \xrightarrow{\text{Electrolysis}} H^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)}$$

At cathode: $2H^{\oplus}_{(aq)} + 2e^{\ominus} \longrightarrow H_2\uparrow_{(g)}$

At anode: $2Cl^{\ominus}_{(aq)} \longrightarrow Cl_{2(g)} + 2e^{\ominus}$

Similarly, alkali metal halides liberate alkali metals at the cathode on electrolysis.

$$NaCl_{(aq)} \longrightarrow Na^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)}$$

At cathode: $Na_{(aq)} + e^{\ominus} \longrightarrow Na_{(aq)}$

At anode: $2Cl^{\ominus}_{(aq)} \longrightarrow Cl_2 + 2e^{\ominus}$

3.3.1.2 Differences Between Hydrogen and Alkali Metals

1. **Ionisation enthalpy:** Both have one electron in their valence shell, but the ionisation enthalpy of hydrogen is very high as compared to that of alkali metals, i.e. *hydrogen is comparatively less electropositive than alkali metals.*
2. **Difference in the physical state:** Hydrogen exists as a gaseous diatomic molecule (H_2), whereas alkali metals are solids.
3. **Ionic radii:** The ionic radii of $H^{\oplus}$ ion is much less as compared to those of alkali metal ions.

   Due to its small size, $H^{\oplus}$ does not exist freely and is always associated with other atoms or molecules, in aqueous solution, $H^{\oplus}$ ion exists as hydrated proton $[H_9O_4]^{\oplus}$ in which four H_2O molecules are tetrahedrally arranged around the $H^{\oplus}$ ion. However, hydrated $H^{\oplus}$ ion is generally written as $[H_3O]^{\oplus}$ and is known as hydronium ion.
4. **Nature of oxides:** Oxide of hydrogen, i.e. H_2O is neutral, while those of alkali metals are basic.
5. **Nature of halides:** With halogens, hydrogen forms halides, namely HF, HCl, HBr and HI which are low boiling covalent compounds, whereas alkali metals form NaCl, NaBr, KBr etc. which are high melting ionic solids.

3.3.2 COMPARISON WITH HALOGENS

3.3.2.1 Similarities Between Hydrogen and Halogens

1. **Electronic configuration:** Hydrogen has one electron in its valence shell and thus is short of one electron to attain the stable electronic configuration of next noble gas, He. Similarly, halogens have seven electrons in their valence

shell and thus are short of one electron to attain the stable electronic configuration of next noble gas.

2. **Electronegative character:** Both hydrogen and halogens have a tendency to gain one electron to form hydride ion ($H^{\ominus}$) and halide ions ($X^{\ominus}$).

$$H + e^{\ominus} \longrightarrow H^{\ominus}$$
$$(1s^1) \qquad (1s^2)$$
$$F + e^{\ominus} \longrightarrow F^{\ominus}$$
$$(2s^2\,2p^5) \qquad (2s^2\,2p^6)$$

3. **Ionisation enthalpy:** They have comparable ionisation enthalpies.
4. **Oxidation state:** Both exhibit an oxidation state of –1.

$\overset{\oplus}{Na}H^{\ominus} \qquad \overset{\oplus}{Na}Cl^{\ominus}$

5. **Atomicity and non-metallic character:** Both exist as diatomic molecules, e.g. H_2, F_2, Cl_2, Br_2 and I_2. Both hydrogen and halogens are typical non-metals.
6. **Affinity for metals:** Both combine with highly electropositive alkali and alkaline earth metals to form metallic hydrides and metallic halides, respectively.

$$2Na + H_2 \longrightarrow 2NaH$$
$$2Na + Cl_2 \longrightarrow 2NaCl$$

7. **Affinity for non-metals:** Both react with non-metals such as C, Si, Ge, to form covalent compounds.

With hydrogen:	CH_4	SiH_4	GeH_4
With halogen:	CCl_4	$SiCl_4$	$GeCl_4$

8. **Liberation at the anode:** On electrolysis, fused alkali metal hydrides (e.g. LiH) liberate H_2 at the anode. Similarly, when fused alkali metal halide is electrolysed, halogen is liberated.

$$\begin{array}{lcc} & \text{At cathode} & \text{At anode} \\ 2LiH \xrightarrow{\text{Electrolysis}} & 2Li \quad + & H_{2(g)} \\ 2LiCl \xrightarrow{\text{Electrolysis}} & 2Li \quad + & Cl_{2(g)} \end{array}$$

This shows that hydrogen as well as halogens both have electronegative character.

9. **Substitution or replacement reaction:** Hydrogen can be replaced by halogen or vice versa in compounds such as hydrocarbons. This indicates the similar nature of hydrogen and halogens.

$$CH_4 + Cl_2 \xrightarrow[\text{sunlight}]{\text{Diffused}} CH_3Cl + HCl$$
$$CH_3Cl + [H] \xrightarrow{Sn/HCl} CH_4 + HCl$$

3.3.2.2 Differences Between Hydrogen and Halogens

1. **Electronic configuration:** Unlike halogens, hydrogen contains only one proton and no neutron in its nucleus and only one electron in the extranuclear part.
2. **Nature of oxides:** Oxide of hydrogen (H_2O) is neutral whereas oxides of halogens are acidic (Cl_2O_7).
3. **Electronegativity:** Hydrogen has less tendency to gain electron and form uninegative ion $H^{\ominus}$, whereas halogens have strong tendency to form halide ions.

3.3.2.3 Similarities Between Hydrogen and Carbon

1. **Electronic configuration:** Outer shells of both hydrogen and carbon are half filled.
2. **Electronegativity:** Both have similar values of electronegativity. On the other hand, the electronegativity of hydrogen differs from the alkali metals as well as halogens.
3. **Bad conductor of electricity:** Hydrogen in the liquid state does not conduct electricity as its electrons are not sufficiently mobile. Similarly, carbon (except graphite) is a bad conductor of electricity.
4. **Formation of covalent compounds:** Both hydrogen and carbon do not show any readiness to form positive ion or negative ion, rather they form covalent compounds. Normal covalency of hydrogen is one and that of carbon is four.

3.3.3 Unique Position of Hydrogen

From the above discussion, it is clear that there are some resemblances in the properties of hydrogen with alkali metals and halogens, at the same time it differs from both of them in certain properties. Therefore, it is not justified to place hydrogen along with the elements of group 1, or group 17. In some of its properties, hydrogen resembles carbon.

Mendeleev, in his periodic table, had placed hydrogen isolated from other elements due to its unique properties. In the long form of periodic table or *Modern periodic table*, hydrogen has been placed with group 1 elements to indicate its distinctive character.

3.4 DIHYDROGEN (H_2)

3.4.1 Occurrence

Hydrogen is the most abundant element in the universe (70% of the universe's total mass). The giant planets, namely Jupiter and Saturn consist mostly of hydrogen. About half the mass of the sun and some other stars is made up of hydrogen. It is *the third most abundant element on the surface of the globe*. In the combined form it constitutes 15.4% of the earth's crust and the oceans. In the combined form besides water, it occurs in plant and animal tissues, carbohydrates, proteins, hydrides including hydrocarbons and other compounds. *On the earth, hydrogen is the ninth element in order of abundance* and forms 0.9% of the earth's crust by weight. *In the crustal rocks, it is tenth in the order of abundance*, i.e. ~0.15% by weight.

Dihydrogen (H_2) is not found in our atmosphere, as H_2 molecules are very light and the earth does not possess gravitational pull to retain them.

3.4.2 Isotopes of Hydrogen

Naturally occurring hydrogen has three isotopes:

1. Protium or ordinary hydrogen: ${}_1^1H$
2. Deuterium or heavy hydrogen: ${}_1^2H$ or D
3. Tritium: ${}_1^3H$ or T

Table 3.1 Isotopes of hydrogen

Isotope	Protons (p) $p = Z$	Neutrons (n) $n = A - Z$
Protium	1	0
Deuterium	1	1
Tritium	1	2

The three isotopes differ from one another in terms of neutrons. Protium, deuterium and tritium have 0, 1 and 2 neutrons in their nucleus, respectively. The structure of these three isotopes of hydrogen in terms of number of proton, neutron and electron is given in Fig. 3.1.

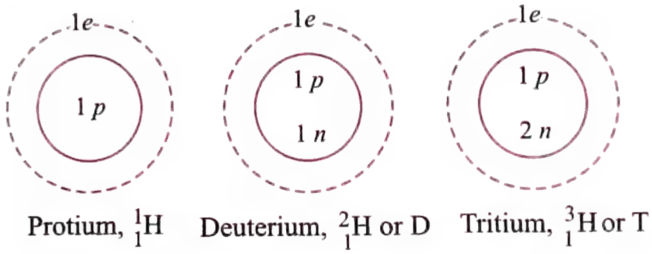


Fig. 3.1 Structure of isotopes of hydrogen

As these three isotopes have same atomic number and electronic configuration, they have essentially the same chemical properties. Certain chemical properties in which they differ are as follows :

1. Rates of reaction
2. Equilibrium constants, for example H_2 is more easily adsorbed than D_2 on activated charcoal.
3. Reaction between H_2 and Cl_2 is more than 13 times faster than between D_2 with Cl_2, as the activation energy of H_2 is much less than D_2.
4. Electrolysis of H_2O occurs more rapidly as compared to D_2O (heavy water).

The above-mentioned differences are due to the difference in the atomic mass of the isotopes. *The differences in properties due to the difference in mass are called isotope effects.*

As the isotopes have different masses, there is considerable difference in their physical properties, since the percentage of difference in mass between protium, deuterium and tritium is greater than between the isotopes of any other element, the isotopes of hydrogen show much greater difference in physical properties than found between the isotopes of other elements.

The term *dihydrogen* is used for H_2 molecule, while referring to the isotopic mixture with natural abundance for H and D. For H_2, the correct term is *diprotium.*
Similarly, proton is used for $H^{\oplus}$ and *hydron* is used in relation to the isotopic mixture.

3.4.3 Preparation of Dihydrogen (H_2)

The main sources from which dihydrogen can be prepared are water, acids and alkalis.

Metals which are more electropositive than hydrogen, displace H_2 gas from water.

1. **From water**
   a. **Water at ordinary or room temperature:** Metals having very low standard of reduction potentials, e.g. alkali metals and certain alkaline earth metals (Ca, Sr, Ba) are very active and decompose water at room temperature, thus liberating dihydrogen gas.

   $2Na + 2H_2O \longrightarrow 2NaOH + H_2\uparrow$

   $Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2\uparrow$

   The reaction between alkali metals and water is highly vigorous and exothermic, and the H_2 evolved catches fire. To slow down the reaction, amalgams (alloy with mercury) of alkali metals are used. In the amalgams, since a small area of alkali metal comes into contact with water, hence the reaction slows down.

   b. **Boiling water:** Less active metals such as magnesium powder, zinc powder, aluminium powder etc. decompose boiling water to liberate H_2 gas.

   $Mg + H_2O \xrightarrow{\Delta} Mg(OH)_2 + H_2\uparrow$

   $Zn + H_2O \xrightarrow{\Delta} Zn(OH)_2 + H_2\uparrow$

   $2Al + 3H_2O \xrightarrow{\Delta} Al_2O_3 + H_2\uparrow$

   c. **Steam:** Still less active metals such as iron, nickel, tin etc. decompose steam at high temperature. However, the reaction with iron is reversible.

   $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$

2. **From acids:** Metals such as zinc, iron, magnesium etc. which are more electropositive than hydrogen, i.e. lie above hydrogen in the electrochemical series, react with dilute mineral acids (dil H_2SO_4 and dil HCl).

   $Zn + \underset{\text{dil}}{H_2SO_4} \longrightarrow ZnSO_4 + H_2\uparrow$

   $Fe + 2HCl \longrightarrow FeCl_2 + H_2\uparrow$

   Whereas metals such as copper, silver, mercury etc. which are less electropositive than hydrogen, i.e. lie below hydrogen in the electrochemical series, do not react with mineral acids.

3. **From alkalis:** Metals such as beryllium, aluminium, tin, zinc, etc., react in hot solution of alkalis to liberate H_2 gas.

   $Be + 2NaOH \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2} + H_2$

   $Al + NaOH \longrightarrow \underset{\text{Sodium meta-aluminate}}{Na_2AlO_2} + 3H_2$

   $Sn + 2NaOH + H_2O \longrightarrow \underset{\text{Sodium stannate}}{Na_2SnO_3} + 2H_2$

   $Zn + 2NaOH \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2$

3.4.3.1 Preparation of Pure Dihydrogen Gas

Pure dihydrogen (>99.95%) required for military purpose can be produced on the spot as follows:

1. By the action of water on LiH or NaH or CaH_2.

$$LiH + H_2O \longrightarrow \underset{\text{Lithuim hydroxide}}{LiOH} + H_2\uparrow$$

$$NaH + H_2O \longrightarrow \underset{\text{Sodium hydroxide}}{NaOH} + H_2\uparrow$$

$$CaH_2 + H_2O \longrightarrow \underset{\text{Calcium hydroxide}}{Ca(OH)_2} + H_2\uparrow$$

2. Uyeno's method: By heating Al shavings or scrap with NaOH or KOH solution.

$$2Al + 2KOH + 2H_2O \longrightarrow 2KAlO_2 + 3H_2\uparrow$$

3. By the action of water on *hydrone* (an alloy of Na and Pb).

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

4. By treating powdered *ferrosilicon* (an alloy containing 90% Si and 10% Fe) with hot NaOH solution (20%).

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$

5. By the action of pure dil H_2SO_4 on Mg ribbon.

$$Mg + \underset{\text{(dil)}}{H_2SO_4} \longrightarrow MgSO_4 + H_2\uparrow$$

6. By electrolysis of warm solution of barium hydroxide, $Ba(OH)_2$, using platinum or nickel electrodes.

3.4.3.2 Commercial Production or Manufacture of Dihydrogen

1. **By the electrolysis of water:** A small amount of an acid, e.g. H_2SO_4 or an alkali, e.g. NaOH (15–25%) is added to water and electrolysed in a cell in which iron sheet is used as a cathode and nickel-plated iron sheet is used as anode. *Addition of an acid or an alkali to water makes water a good conductor of electricity.* The anode and cathode are separated by a porous asbestos diaphragm, hence the mixing of dihydrogen and dioxygen is prevented. On electrolysis, dihydrogen is collected at anode, whereas dioxygen is liberated as a by-product at anode.

$$H_2O \rightleftharpoons H^{\oplus} + \overset{\ominus}{O}H$$

At cathode: $H^{\oplus} + e^{\ominus} \longrightarrow H$

$$H + H \longrightarrow H_2\uparrow$$

At anode: $4\overset{\ominus}{O}H \longrightarrow 4OH + 4e^{\ominus}$

$$4OH \longrightarrow 2H_2O + O_2\uparrow$$

Dihydrogen produced by this method is very high. This is the best method to produce dihydrogen, if electricity is cheap.

2. **Lane's process:** By passing alternate currents of steam and water gas over red hot iron, dihydrogen is obtained. In other words, this process consists of two steps:

a. **Oxidation:** Superheated steam is passed into vertical retorts packed with iron filings, maintained at 1023–1073 K in a suitable furnace. Iron gets converted into its magnetic oxide, Fe_3O_4 and H_2 is liberated.

$$3Fe + 4H_2O \xrightarrow{1023\text{–}1073\,K} Fe_3O_4 + 4H_2\uparrow + 160.7\ kJ$$

b. **Reduction:** Iron is regenerated by reducing Fe_3O_4 by any reducing gas. Water gas ($CO + H_2$) is used in Lane's process.

$$Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$$

$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2\uparrow$$

3. **Bosch's process (from water gas):** The largest quantity of commercial H_2 gas is prepared from water gas. This method involves the following steps:

a. **Preparation of water gas:** On passing steam through a mass of red hot coke or coal at 1273 K, in the presence of Ni as catalyst, water gas, i.e. a mixture of CO and H_2 is produced.

$$\underset{\text{Coke}}{C_{(s)}} + \underset{\text{Steam}}{H_2O_{(g)}} \xrightarrow[\text{Ni catalyst}]{1273\,K} \underbrace{CO_{(g)} + H_{2(g)}}_{\text{Water gas}}$$

In earlier days, a 1:1 mixture of CO and H_2 was referred to as water gas, but nowadays, a mixture of CO and H_2 in any ratio is called *synthesis gas* or *syngas*. Since a mixture of CO and H_2 is used for synthesis of methanol and a number of hydrocarbons, it is known as syngas. The process by which syngas is produced from coke or coal is known as *coal gasification*. Syngas can also be produced from sewage, sawdust, scrap wood, newspapers etc.

b. **Separation of CO from water gas:** As removal of CO from water gas is difficult, therefore to separate H_2 from water, CO is oxidised to CO_2. This is done by mixing water gas with twice of its volume with steam at 673K in the presence of iron chromate, ($FeCrO_4$) as catalyst. $FeCrO_4$ helps in oxidation of CO to CO_2.

$$\underbrace{H_2 + CO}_{\text{Water gas}} + H_2O \xrightarrow[\text{FeCrO}_4\ \text{Catalyst}]{673\,K} CO_2 + 2H_2\uparrow$$

This reaction is known as *water gas shift reaction*. The mixture of CO_2 and H_2 is passed through water under a pressure of 25–30 atm, when CO_2 dissolves completely in water,

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

while H_2 gas passes on and is collected. Traces of CO present in H_2 are removed by passing the gas at 200 atm through ammonical cuprous formate solution in which CO is soluble.

4. **Steam reforming of hydrocarbons:** Dihydrogen gas on a massive industrial scale is nowadays prepared by steam reforming process. It involves reaction between steam and hydrocarbons from natural gas or petroleum at high temperature and pressure in the presence of Ni catalyst to

form CO and H_2. Natural gas mainly consists of methane, CH_4.

$$\underset{}{CH_{4(g)}} + \underset{\text{Steam}}{H_2O_{(g)}} \xrightarrow[\text{Ni catalyst}]{1270\text{ K}} \underbrace{CO + 3H_2\uparrow}_{\text{Syn gas}}$$

H_2 gas, thus obtained, is separated from syngas by Bosch's process.

5. **Thermal cracking of natural gas:** Dihydrogen gas can also be obtained by thermal cracking of natural gas.

$$CH_4 \xrightarrow[\text{Catalyst}]{1270\text{ K}} C + 2H_2$$

6. **As a by-product:** Large quantities of H_2 gas are obtained as a by-product in various industries. For example,
   a. Catalytic cracking of higher hydrocarbons in petroleum cracking plants.

   $$\underset{n\text{-Heptane}}{C_6H_{14}} \longrightarrow \underset{\text{Benzene}}{C_6H_6} + 4H_2\uparrow$$

   b. In the manufacture of sodium hydroxide and chlorine using brine solution (refer to Chapter 4).
7. Relative smaller quantities of H_2 gas (1–17 $m^3\ h^{-1}$) are obtained by passing a 1:1 molar mixture of vapourised methonol and water over a 'base-metal chromite' type catalyst at 673 K. The mixture of dihydrogen and carbon monoxide obtained is made to react with steam to give CO_2 and more dihydrogen.

$$CH_3OH \xrightarrow[\text{Catalyst}]{673\text{ K}} CO + 2H_2$$

$$CO + \underset{\text{Steam}}{H_2O} \xrightarrow[\text{Catalyst}]{673\text{ K}} CO_2 + H_2$$

3.4.4 Properties of Dihydrogen (H_2)

3.4.4.1 Physical Properties

1. Dihydrogen is a colourless, odourless, combustible and tasteless gas.
2. It is lighter than air. At NTP, 1 L of H_2 weighs 0.0899 g. Its density is ~ 1/14th of that of air.
3. It is almost insoluble in water due to its non-polar nature.
4. It can be liquefied under low temperature and high pressure.

Some common physical properties of dihydrogen (H_2) are given along with those of dideuterium (D_2) and ditritium (T_2).

3.4.4.2 Chemical Properties

Dihydrogen is not very reactive under normal conditions. This is largely due to its high bond dissociation enthalpy. For H_2 to react with any other element compound, breaking of H–H bond to produce hydrogen atoms is required. This requires 435.9 kJ mol^{-1}, which is the highest for a single bond between two atoms of any element.

$$\underset{\text{Dihydrogen}}{H_{2(g)}} \longrightarrow \underset{\text{Atomic hydrogen}}{2H_{(g)}} \qquad \Delta_{diss}H^\ominus = 435.9\text{ kJ mol}^{-1}$$

Thus H_2 molecule is quite stable and relatively inert under normal conditions due to its high bond dissociation enthalpy. Consequently, many reactions are slow or require high temperature or catalysts.

However, at high temperature, in an electric arc or under UV (ultra-violet) light, H_2 does dissociate to produce *atomic hydrogen*. As the electronic configuration of atomic hydrogen is $1s^1$, it needs one electron to complete its orbital, and thus is quite reactive. The atomic hydrogen produced exists for less than half a second and then it recombines to give dihydrogen and large amount of heat.

Some of the important chemical properties of dihydrogen are as follows:

1. **Reaction with dioxygen:** It burns in air or dioxygen with pale blue flame forming water. In this process, large amount of heat is liberated. H_2 gas is higly combustible but a non-supporter of combustion.

   $$2H_2 + O_2 \longrightarrow 2H_2O \qquad \Delta_f H^\ominus = -485\text{ kJ mol}^{-1}$$

   This is used in oxy-hydrogen flame for welding and cutting metals, as temperature of almost 3000°C can be attained. Care should be taken while handling these gases, since the mixture of H_2 and O_2 close to 2:1 ratio is often explosive.
2. **Reaction with metals:** Dihydrogen reacts with higly electropositive metals such as lithium, sodium and calcium to give ionic (or salt-like) hydrides... (refer to section 3.6.1).
3. **Reaction with non-metals:** Dihydrogen reacts with many non-metals at high temperature or in the presence of catalyst to give covalent or molecular hydrides.
   a. **With halogen:** H_2 combines with halogens (X_2) to form halogen hydracids.

   $$H_{2(g)} + X_{2(g)} \longrightarrow 2HX_{(g)} \qquad (X = F, Cl, Br, I)$$

   The reactivity of halogens towards dihydrogen is

   $F_2 > Cl_2 > Br_2 > I_2$

   Thus, fluorine (F_2) reacts instantly even in dark with explosive voilence, Cl_2 reacts at room tempertaure in the presence of sunlight or at 670 K or above. Br_2 reacts with H_2 on heating while I_2 reacts with H_2 on heating in the presence of a catalyst.

   $$H_{2(g)} + F_{2(g)} \xrightarrow{\text{Dark}} \underset{\text{Hydrogen fluoride}}{2HF_{(g)}}$$

   $$H_{2(g)} + Cl_{2(g)} \xrightarrow[\text{sunlight}]{\text{Diffused}} \underset{\text{Hydrogen chloride}}{2HCl}$$

   $$H_{2(g)} + Br_{2(g)} \xrightarrow{670\text{ K}} \underset{\text{Hydrogen bromide}}{2HBr_{(g)}}$$

   $$H_{2(g)} + I_{2(g)} \xrightarrow[\text{Pt}]{670\text{ K}} \underset{\text{Hydrogen iodide}}{2HI_{(g)}}$$

   b. **With nitrogen (N_2):** H_2 combines with N_2 under high pressure, in the presence of iron as catalyst and molybdenum as promoter.

   $$N_{2(g)} + 3H_{2(g)} \underset{\text{Fe, Mo}}{\overset{673\text{ K, 200 atm}}{\rightleftharpoons}} 2NH_3 \qquad \Delta_f H^\ominus = -92.6\text{ kJ mol}^{-1}$$

   This reaction is used to manufacture ammonia, NH_3, by Haber's process.

c. **With carbon:** H_2 combines with carbon at 1420 K to form methane in small quantities.

$$2H_2 + C \xrightarrow{1420\text{ K}} \underset{\text{Methane}}{CH_4}$$

d. **With sulphur, selenium and tellurium:** H_2 forms respective hydrides on heating from 470 to 670 K.

$$H_{2(g)} + S_{(l)} \longrightarrow H_2S_{(g)}$$

4. **Reducing agent:** Dihydrogen acts as strong reducing agent and reduces metal oxides and ions to metal. When dihydrogen gas is passed over heated metallic oxides, it removes oxygen from them and combines with it to form water. The process of removal of oxygen from a compound is called reduction, while the substances, e.g. H_2, which bring about reduction are called reducing agents.

$$CuO + H_2 \xrightarrow{\Delta} Cu + H_2O$$

$$ZnO + H_2 \xrightarrow{\Delta} Zn + H_2O$$

The oxides of strongly electropositive metals such as alkali and alkaline earth metals are not reduced by this method.

Metal ions in aqueous solution are also reduced by dihydrogen.

$$Cu^{\oplus}_{(aq)} + H_{2(g)} \longrightarrow Cu_{(s)} + 2H^{\oplus}_{(aq)}$$

5. **Hydrogenation:** In the presence of finely divided nickel, dihydrogen acts as good reducing agent. H_2 combines with unsaturated organic compounds, e.g. alkenes and alkynes and converts them into alkanes in the presence of a catalyst.

$$\underset{\text{Acetylene}}{HC \equiv CH} + H_2 \xrightarrow[473\text{ K}]{\text{Ni or Pd or Pt}} \underset{\text{Ethylene}}{H_2C = CH_2} \xrightarrow[473\text{ K}]{\text{Ni or Pd or Pt}} \underset{\text{Ethane}}{H_3C - CH_3}$$

Dihydrogen finds use in many industrial processes such as hydrogenation of unsaturated organic compounds in the presence of homogeneous and heterogeneous catalysis. The examples are as follows :

Hydroformylation of olefins:

$$\underset{\text{Olefins}}{RCH = CH_2} + CO + H_2 \xrightarrow{[Co(CO)_4]_2} \underset{\text{Aldehyde}}{RCH_2CH_2CHO}$$

Olefins react with carbon monoxide and dihydrogen in the presence of $[Co(CO)_4]_2$ catalyst under high temperature and pressure to form aldehyde. This reaction is also known as hydroformylation or oxo-process. The aldehyde thus obtained undergoes further reduction and gives alcohol.

$$\underset{\text{Aldehyde}}{RCH_2CH_2CHO} + H_2 \xrightarrow{Ni} \underset{\text{Alcohol}}{RCH_2CH_2CH_2OH}$$

3.4.5 Uses of Dihydrogen

The uses of dihydrogen are as follows:

1. In chemical industries, to synthesise ammonia (NH_3) by Haber's process, which is used in the production of fertilisers, urea, ammonium sulphate, calcium ammonium nitrate (CAN) etc.
2. In the manufacture of bulk organic chemicals, particulary methanol.

$$\underbrace{CO_{(g)} + H_{2(g)}}_{\text{Water gas}} + H_{2(g)} \longrightarrow \underset{\text{Methanol}}{CH_3OH_{(l)}}$$

3. In the manufacture of vanaspati ghee by the hydrogenation of polyunsaturated vegetable oils such as coconut oil, cottonseeds, soyabean etc.
4. In the manufacture of metal hydrides.
5. In metallurgy, to produce pure metals from their oxides.
6. As a fuel in rockets (liquid hydrogen mixed with liquid oxygen) and guided missiles.
7. In the manufacture of hydrogen chloride, a highly useful chemical.
8. In atomic hydrogen (produces temperature~400 K) and oxy-hydrogen torches (produces temperature in the range of 2270–2770 K) for cutting and welding purpose, for melting platinum and quartz.
9. In fuel cells to generate electrical energy. H_2 is better fuel than conventional fossil fuels and electric power as:
   a. It does not produce any pollution.
   b. It releases greater energy per unit mass of fuel as compared to other fuels.

ILLUSTRATION 3.1

Comment on the reactions of dihydrogen with (a) chlorine, (b) sodium and (c) copper (II) oxide.

Sol.

a. Dihydrogen reduces chlorine into chloride ($Cl^{\ominus}$) ion and itself gets oxidised to $H^{\oplus}$ ion by chlorine to form hydrogen chloride. An electron pair is shared between H and Cl leading to the formation of a covalent molecule.

$$H_{2(g)} + Cl_{2(g)} \longrightarrow \underset{\text{Hydrogen chloride}}{2HCl_{(g)}}$$

b. Dihydrogen is reduced by sodium to form NaH. An electron is transferred from Na to H leading to the formation of an ionic compound, $Na^{\oplus}H^{\ominus}$.

$$H_{2(g)} + 2Na_{(s)} \longrightarrow \underset{\text{Sodium hydride}}{2NaH_{(s)}}$$

c. Dihydrogen reduces copper (II) oxide to copper in zero oxidation state and itself gets oxidised to H_2O, which is a covalent molecule.

$$H_{2(g)} + CuO \longrightarrow Cu_{(s)} + H_2O_{(l)}$$

ILLUSTRATION 3.2

a. Would you expect the hydrides of N, O and F to have lower boiling points than the hydrides of their subsequent group members? Give reason.

b. Can phosphorous with outer electronic configuration $3s^2\,3p^3$ form PH_5?

c. How many hydrogen-bonded water molecule(s) are associated with $CuSO_4{\cdot}5H_2O$?

Sol.

a. On the basis of molecular masses of NH_3, H_2O and HF, their boiling points are expected to be lower than those of the subsequent group member hydrides. However, due to higher electronegativity of N, O and F, the magnitude of hydrogen bonding in their hydrides will be quite appreciable. Hence, the boiling points of NH_3, H_2O and HF will be higher than the hydride of their subsequent group members.

b. Although phosphorous exhibits +3 and +5 oxidation states, it cannot form PH_5. Besides some other considerations, high $\Delta_a H$ value of dihydrogen and $\Delta_{eg}H$ value of hydrogen do not favour to exhibit the highest oxidation state of P and consequently the formation of PH_5.

c. Copper sulphate, $CuSO_4 \cdot 5H_2O$ can be represented as $[Cu(H_2O)_4]^{2+} SO_4^{2-} \cdot H_2O$

Only one water molecule, which is present outside the coordination sphere, i.e. square bracket is hydrogen bonded. The other four water molecules are bonded to Cu^{2+} by coordinate bond.

ILLUSTRATION 3.3

a. Which isotope of hydrogen is used as a tracer in organic reactions?

b. Concentrated H_2SO_4 cannot be used for drying H_2. Why?

c. The electrolysis of water for manufacturing H_2 gas is always carried out in the presence of acid (H_2SO_4) or alkali (KOH), yet no SO_4^{2-} or $K^{\oplus}$ are discharged. Why?

Sol.

a. Hydrogen has three isotopes: protium or hydrogen, ${}^1_1H$; deuterium (${}^2_1H$ or D) and tritium (${}^3_1H$ or T). Due to the difference in masses, the rate constants of these isotopes with the same substrate are different. In other words both D and T show isotope effect. Since T is not only radioactive but is also least abundant hydrogen isotope, therefore D is used as a tracer to study the mechanism of organic reactions.

b. Conc H_2SO_4 on absorbing water (H_2O) from moist H_2 produces so much heat that H_2 catches fire.

c. Sulphate and potassium ions are not discharged as the discharge potential of SO_4^{2-} ion is much higher than $\overset{\ominus}{O}H$ ion and the discharge potential of $K^{\oplus}$ ion is much higher than $H^{\oplus}$ ion.

ILLUSTRATION 3.4

a. A solution of ferric chloride acidified with HCl is unaffected when hydrogen is bubbled through it, but gets reduced when zinc is added to acidified solution. Explain.

b. When sodium hydride in fused state is electrolysed, hydrogen is discharged at the anode. Explain.

Sol.

a. Molecular hydrogen is not so reactive as nascent hydrogen. Zinc reacts with the acid to produce nascent hydrogen which reduces ferric chloride into ferrous chloride.

b. Sodium hydride, NaH, is an electrovalent compound in which hydrogen is present as an anion, $H^{\ominus}$. On electrolysis, it is discharged at anode.

$$NaH \rightleftharpoons Na^{\oplus} + H^{\ominus}$$

$$\text{At cathode: } Na^{\oplus} + e^{\ominus} \longrightarrow Na$$

$$\text{At anode: } H^{\ominus} \longrightarrow H + e^{\ominus}$$

$$2H \longrightarrow H_2\uparrow$$

ILLUSTRATION 3.5

In the laboratory, for the preparation of dihydrogen gas from granular zinc, conc H_2SO_4, conc HCl and HNO_3 cannot be used. Why? Which is the most suitable acid?

Sol. For the prepartion of dihydrogen gas from granular zinc, conc H_2SO_4, conc HCl and HNO_3 cannot be used due to:

a. A part of conc H_2SO_4 reacts with H_2 and gets reduced to sulphur dioxide, SO_2

$$\underset{\text{conc}}{H_2SO_4} + H_2 \longrightarrow 2H_2O + SO_2\uparrow$$

b. When conc HCl is used, dihydrogen liberated by the action of conc HCl on granular zinc will be impure as it contains fumes of volatile HCl. Moreover, $ZnCl_2$ formed is insoluble in conc HCl. It forms a coating on granular zinc and the reaction stops after sometime.

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2\uparrow$$

HNO_3 acts both as an acid and as an oxidising agent. The nascent hydrogen first formed reduces the nitric acid into various oxides.

$$2HNO_3 + 2H \longrightarrow 2NO_2 + 2H_2O$$

$$2HNO_3 + 6H \longrightarrow 2NO + 4H_2O$$

The most suitable acid is dilute H_2SO_4.

3.5 VARIOUS FORMS OF HYDROGEN

3.5.1 Nascent Hydrogen

When H_2 gas is bubbled through acidified potassium permanganate $KMnO_4$, colour is not discharged. But on addition of some zinc pieces to the above solution, tiny bubbles of hydrogen are found to rise and $KMnO_4$ gets decolourised. Hydrogen produced, in situ in the second case is more active than molecular hydrogen, H_2, and is known as nascent hydrogen (newly born).

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + \underset{\substack{\text{Nascent}\\\text{hydrogen}}}{2H}$$

$$2KMnO_4 + 3H_2SO_4 + 10H \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$$

Similarly, ferric chloride (yellow) gets decolourised by the addition of zinc pieces and hydrochloric acid. This is also due to reduction of ferric chloride to ferrous chloride (faint green solution) by nascent hydrogen.

$$Zn + 2HCl \longrightarrow ZnCl_2 + 2H$$

$$FeCl_3 + H \longrightarrow FeCl_2 + HCl$$

Nascent hydrogen can also be prepared by the

- action of water on sodium amalgam

$$Na + H_2O \longrightarrow NaOH + H$$

- action of NaOH on Zn or Al

$$Zn + 2NaOH \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + 2H$$

It is believed that a part of energy liberated in the reaction producing hydrogen becomes associated with hydrogen molecules and this makes them hyperactive.

3.5.2 Adsorbed or Occluded Hydrogen

Graham (1867) found that one volume of red hot palladium on cooling adsorb 975 volume of hydrogen. The gas thus adsorbed by the metal is given off when the metal is heated, especially under reduced pressure. This phenomenon was named as occlusion or adsorption by Graham. The gas so adsorbed by the metal is called occluded or adsorbed hydrogen. Some other metals such as Pt, Au, Fe, Ni, etc. also exhibit this phenomenon.

Occluded hydrogen is more active and a stronger reducing agent than ordinary hydrogen. Recently, it is believed that occluded hydrogen gives an interstitial compound in which hydrogen occupies the holes in the crystal lattice of the metal.

3.5.3 Atomic Hydrogen

Langmuir (1922) showed that when molecular hydrogen in contact with tungsten or platinum wire was heated by an electric current at low pressure, it gets dissociated into atomic hydrogen. This is an endothermic process and requires +104.5 kcal mol^{-1}.

$$\underset{\text{Molecular hydrogen}}{H_2} \longrightarrow \underbrace{H + H}_{\text{Atomic hydrogen}} - 104.5\ \text{kcal mol}^{-1}$$

The atomic hydrogen thus produced was found to be more reactive than ordinary, nascent and adsorbed hydrogen.

The life period of atomic hydrogen is only 1/3rd of a second, but under certain circumstances can be extended to 10 seconds.

Atomic hydrogen being extremely unstable quickly combines to give molecular hydrogen. Metals such as Pt, Pd etc. accelerate this recombination.

$$H + H \rightleftharpoons H_2 + 104.5\ \text{kcal mol}^{-1}$$

This exothermic reaction is used in *atomic hydrogen welding torch*, which is employed for the welding of cracked metals such as Mn, Cr, W etc.

In atomic hydrogen welding torch, when H_2 is passed through an electric arc struck between two tungsten electrodes, the H_2 molecule adsorbs heat and dissociates to give active hydrogen.

$$H_2 \xrightarrow{\text{Heat}} 2H$$

Just beyond the arc, active hydrogen recombines to form and evolve the heat which they have previously adsorbed.

$$2H \longrightarrow H_2 + \text{Heat}$$

The heat thus generated and the heat of burning hydrogen creates a high temperature (~5000°C) and this is used for welding the cracked metals and for melting some of the most refractory materials such as W, Ta, ThO_2 etc.

3.5.4 Ortho- and Para-hydrogen (Spin Isomers)

The hydrogen molecule exists in two different forms: (a) ortho-hydrogen and (b) para-hydrogen. These are known as nuclear spin isomers.

When the nucleus of an atom contains an odd number of nucleons, the nucleus has a resultant spin. If two such atoms combine to form a diatomic molecule, the nuclei may have their spins parallel or antiparallel. This is known as nuclear spin isomerism. The molecule in which the two nuclei have parallel spins are called the ortho-isomer and the molecule with antiparallel nuclear spins is called para-form. Both the forms exist in a temperature-dependent tautomeric equilibrium. Such nuclear spins have been established for H_2, D_2, T_2, ${}^{14}_{2}N$, ${}^{17}_{2}O$ etc.

When two hydrogen atoms combine to form dihydrogen molecule, the two electrons always spin in the opposite direction or otherwise the molecule will not be stable according to Pauli's exclusion principle.

$$H(\uparrow) + H(\downarrow) \longrightarrow H \uparrow\downarrow H \text{ or } H-H \text{ or } H_2$$

The spins of the protons (nuclei) may however either be in the same direction (parallel) or in the opposite direction (antiparallel). When the spins of the nuclei are in the same direction, dihydrogen is called ortho-hydrogen and when the spins are in opposite direction, dihydrogen is called para-hydrogen. The two forms of dihydrogen are shown in Fig. 3.2.

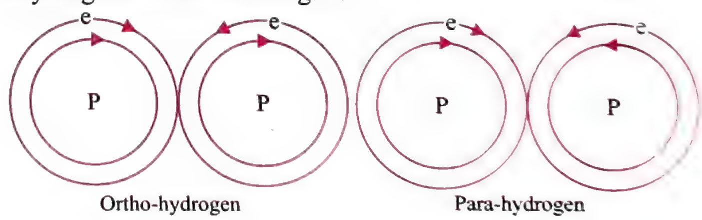


Fig. 3.2 Ortho- and para-hydrogen

The resultant nuclear spins are as follows:

1. Ortho-hydrogen: $+\frac{1}{2} + \frac{1}{2} = +1$; triplet state
2. Para-hydrogen: $+\frac{1}{2} - \frac{1}{2} = 0$; singlet state

It may be noted that the two electrons in the ortho as well as para hydrogen always spin in the opposite direction, otherwise it will not be possible to get stable hydrogen molecule.

Differences between ortho- and para-hydrogen are as follows:

1. **Internal energy:** Para-form has lower internal energy than ortho-form. This difference is due to the fact that in ortho-hydrogen, the spins of the two protons being in same direction, increase the molecular energy of ortho-form. The resultant spin of ortho-hydrogen molecule is 1 (one). Whereas, in para-hydrogen, the spins of the two

protons in opposite direction, cancel each other and thus make the resultant spin as zero. This neutralisation of spins decreases the molecular energy of para-hydrogen. Hence the internal energy of para-hydrogen is lower than that of ortho-hydrogen.

2. **Stability:** Ortho-form is more stable than para-form and hence the para-form has a tendency to change to the ortho-form.
3. **Effect of temperature on the relative proportions of the ortho- and para-hydrogen in ordinary hydrogen:** The relative proportion of ortho- and para-hydrogen, i.e. ortho-para ratio in the ordinary hydrogen depends on the temperature. At *absolute zero*, molecular hydrogen consists only of para-form, i.e. para:ortho form = 1:0, as para-form has lower internal energy.

   With the increase in temperature, the proportion of ortho-form increases and that of para-form decreases. At the temperature of *liquefaction of air*, the ratio of para- and ortho-form is 1:1, while at room temperature and even at elevated temperatures, this ratio is 1:3, as given in Table 3.2.

Table 3.2 Ratio of para and ortho forms at various temperatures

Temperature	% of para-H_2	% of ortho-H_2	Ratio (para:ortho)
At absolute zero	100%	–	1 : 0
At liquefaction of air temperature	50%	50%	1 : 1
At room temperature and at elevated temperature	25%	75%	1 : 3

4. **Physical properties:** Nuclear spin isomerism does not effectively influence the bond between the atoms and hence the chemical properties of ortho- and para-hydrogen (or any other element) are alike (both the forms have same covalent bonding). The physical properties of ortho- and para-hydrogen are not significantly affected by nuclear spin isomerism.

   However some of the notable differences are:

   a. The thermal conducting of para-hydrogen is 50% greater than that of ortho-hydrogen.

   b. The melting point of para-hydrogen is 0.15 K below that of hydrogen containing 75% ortho-H_2.

Para-hydrogen is usually prepared by passing a mixture of ortho and para through a tube packed with charcoal cooled to liquid air temperature. Para-hydrogen, thus prepared can be kept for weeks at room temperature in a glass vessel, as the ortho-para conversion is slow in the absence of catalysts. Some examples of catalysts are atomic hydrogen, activated charcoal, metals such as Fe, Ni, Pt and W and paramagnetic species or ions such as O_2, NO, NO_2, Co^{2+} and Cr_2O_3.

Preparation of pure para-hydrogen: At room temperature, ordinary dihydrogen contains 75% of ortho-hydrogen and 25% of para-hydrogen. As the temperature is lowered, the percentage of ortho-hydrogen in the mixture decreases while that of para-hydrogen increases and at ~20 K, it is pure para-hydrogen. In contrast, when a sample of ordinary hydrogen is heated to say 400 K or above, the ratio of ortho- and para-hydrogen to be remain the same (3:1). *Thus, it is possible to obtain pure para-hydrogen but it is not possible to obtain pure ortho-hydrogen.*

Conversion of para-hydrogen into ortho-hydrogen.

i. By heating para-hydrogen to 800°C or above.

ii. By passing an electric discharge through para-H_2.

iii. By treatment of para-H_2 by catalysts such as Pt, Ni, Fe, W, O_2, NO_2, CO_2, Cr_2O_3.

iv. By mixing para-H_2 with paramagnetic molecules such as O_2 (oxygen), etc.

v. By mixing para-H_2 with atomic hydrogen: Gelb and Herteck have shown that when atomic hydrogen collides with para-H_2; conversion to ortho-H_2 form takes place.

3.6 HYDRIDES

Hydrides can be defined as the binary compounds of the element with hydrogen. Hydrogen forms binary hydrides of the type MH_x or $M_m H_n$ with:

1. All main group elements except the noble gases and probably indium and thallium.
2. All lanthanoids and actinoids.
3. Transition metals—Sc, Y, La, Ac, Zr, Hf and to a lesser extent V, Nb, Ta, Cr, Cu and Zn. Palladium hydride has been extensively studied.

The type of hydride which an element forms depends upon its electronegativity and hence on the type of the bond formed. Based on the physical and chemical properties, the hydrides have been classified as follows:

1. Ionic or salt-like or saline hydrides
2. Covalent or molecular hydrides
3. Metallic or interstitial hydrides

3.6.1 Ionic or Salt-like or Saline Hydrides

Ionic hydrides are formed by group 1 (alkali metals) and heavier group 2 metals (Ca, Sr and Ba), i.e. the most electropositive elements. Ionic hydrides are formed by elements with an electronegativity value appreciably lower than that of hydrogen, i.e. 2.1, thus allowing hydrogen to attract an electron from the metal and form $M^{\oplus}$ and $H^{\ominus}$. These are formed by heating the elements in hydrogen atmosphere at high temperature (595–973 K).

Properties: Some important properties of ionic hydrides are as follows:

1. These compounds are colourless, crystallite solids having high melting point.
2. These are formed by transfer of electron from metal to hydrogen atom and thus are ionic in nature. They contain hydride ion, $H^{\ominus}$. Evidence that they are ionic are:

   a. Molten LiH (mpt 691°C) conducts electricity and H_2 is liberated at the anode, thus confirming the presence of hydride ion, $H^{\ominus}$.

At anode: $2H^{\ominus} \longrightarrow H_{2(g)} + 2e^{\ominus}$

At cathode: $Na^{\oplus} + e^{\ominus} \longrightarrow Na_{(l)}$

b. The other ionic hydrides, except LiH are sufficiently unstable and decompose much before their melting point. When they are dissolved in melt of alkali metal halides (e.g. CaH_2 dissolve in an eutectic mixture of LiCl/KCl) and melt is electrolysed then H_2 gas is liberated at the anode.

c. Crystal structures of these hydrides show no evidence of directional bonding. Alkali metal hydrides have NaCl crystal structure.

3. Density of ionic hydride is higher than that of metal from which it is formed. This is due to the fact that the $H^{\ominus}$ ions occupy the holes in the lattice of the metal, without distorting the metal lattice.

4. Ionic hydrides have high heat of formation and are always stoichiometric.

5. Thermal stability of alkali metal hydrides decreases down the group (↓). This is due to decrease in lattice enthalpy LiH > NaH > KH > RbH >CsH,

   of these hydrides with increase in size of metal cation from $Li^{\oplus}$ to $Cs^{\oplus}$.

   Similarly, the thermal stability of alkaline earth metal hydrides decreases down the group (↓).

   $CaH_2 > SrH_2 > BaH_2$.

6. Alkali metal hydrides are more reactive than corresponding alkaline earth metal hydrides because of large size of cation and less charge, e.g. KH is more reactive than CaH_2. Down the group (↓) reactivity increases due to decrease in stability.

7. **Effect of heat:** Except LiH, ionic hydrides decompose into their constituent elements on strong heating (400–500°C). The dihydrogen produced is highly inflammable, i.e. ignites spontaneously, thus ionic hydrides are used as *solid fuels*.

   $$CaH_2 \xrightarrow{\Delta} Ca + H_2$$

8. **Reaction with protonic solvents:** Ionic hydrides are unstable in protonic solvents (e.g. H_2O, NH_3, C_2H_5OH etc.). They react with the protonic solvent and liberate H_2 gas. Thus they act as strong bases.

   $$LiH_{(s)} + H_2O_{(l)} \longrightarrow LiOH_{(aq)} + H_2$$

   $$CaH_{2(s)} + 2H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)} + 2H_{2(g)}$$

   $$NaH_{(s)} + NH_{3(l)} \longrightarrow NaNH_{2(aq)} + H_{2(g)}$$

   $$LiH_{(s)} + C_2H_5OH_{(l)} \longrightarrow Li(OC_2H_5)_{(aq)} + H_{2(g)}$$

9. **Reducing agents:** Ionic hydrides act as strong reducing agent, especially at high temperatures.

   $$LiH + CO_2 \xrightarrow{\Delta} \underset{\text{Lithium formate}}{HCOOLi}$$

   $$NaH + 2CO \xrightarrow{\Delta} \underset{\text{Sodium formate}}{HCOONa} + C$$

   $$SiCl_4 + 4NaH \xrightarrow{\Delta} \underset{\text{Monosilane}}{SiH_4} + 4NaCl$$

   $$PbSO_4 + 2CaH_2 \xrightarrow{\Delta} \underset{\text{Lead sulphide}}{PbS} + 2Ca(OH)_2$$

   $$4LiH + AlCl_3 \xrightarrow[\text{Reflux}]{\text{Ether}} \underset{\text{Lithuim aluminium hydride}}{LiAlH_4} + 3LiCl$$

   Ionic hydrides are used to prepare important reducing agents such as $LiAlH_4$, $NaBH_4$, which are used in both inorganic and organic synthesis (synthetic chemistry).

   $$4NaH + B(OCH_3)_3 \longrightarrow NaBH_4 + 3NaOCH_3$$

   However, the reactivity of ionic hydrides towards water, (H_2O) limits their usefulness as reducing agents in aqueous medium.

3.6.2 Covalent or Molecular Hydrides

Covalent hydrides are mainly formed by *p*-block elements (except noble gases) and some *s*-block elements (Be and Mg). This is because these elements have high electronegativity and thus the electronegativity difference between these elements and hydrogen will be small.

General formula: XH_n for *s*-block elements

XH_n or XH_{8-n} for *p*-block elements

(where *n* is the group number in the periodic table to which 'X' belongs)

These hydrides usually consist of discrete covalent molecules, which are held together by weak van der Waals forces of attraction and hence are called covalent or molecular hydrides.

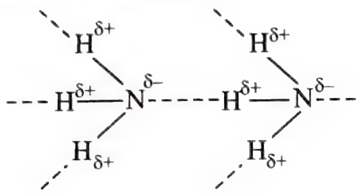
Nomenclature: The systematic names of the molecular hydrides are usually derived from the name of the element and the suffix 'ane', as in phosphane for PH_3, oxidane for H_2O, ozone for NH_3. However, common names such as phosphine, water and ammonia have been used for such a long time in chemistry that scientists are generally reluctant to adopt their systematic names.

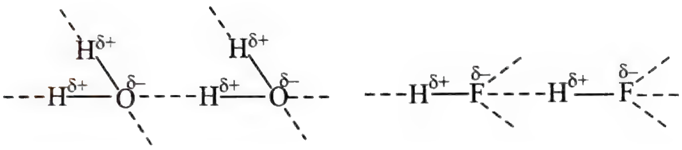
Classification of hydrides: Molecular or covalent hydrides are further classified according to the relative number of electrons and bonds in their Lewis structures as:

1. **Electron-deficient molecular hydrides:** These hydrides have too few electrons as required to write their conventional Lewis structure. In other words, they do not have sufficient number of electrons to form normal covalent bonds and hence are called electron-deficient compounds. They generally exist in polymeric forms. For example, hydrides of group 13 elements [B_2H_6, B_4H_{10}, $(AlH_3)_n$ etc.].

2. **Electron precise or electron exact molecular hydrides:** They have as many number of electrons as required to write their conventional Lewis structures. In other words, they have exact number of electrons required to form normal covalent bonds and hence are called electron precise or electron exact molecular hydrides, for example hydrides of group 14 elements. All these molecules are tetrahedral.

3. **Electron-rich molecular hydrides:** These hydrides have more electrons than required to write their conventional Lewis structures. In other words, they have more electrons than required to form normal covalent bonds and hence are called electron-rich hydrides. Hydrides of group 15, 16 and 17 form electron-rich molecular hydrides. The excess electrons in these hydrides are present as lone pair of electrons. Hydrides of group 15, 16 and 17 have one, two and three lone pair of electrons on highly electronegative O, N and F atoms which result in the formation of intermolecular hydrogen bonds (H-bonds). Consequently, these hydrides exist as associated molecules.





As a result, hydrides of first element of group 15, 16 and 17 have abnormally high boiling points as compared to the boiling points of the hydrides of the rest of element of each group.

Group 15	Hydride	NH_3	PH_3	AsH_3	SbH_3
	b.pt. (K)	238.5	185.5	210.6	254.6
Group 16	Hydride	H_2O	H_2S	H_2Se	H_2Te
	b.pt. (K)	373	213	231	270.8
Group 17	Hydride	HF	HCl	HBr	HI
	b.pt. (K)	292.4	188.0	205.9	237.5

Preparation: Covalent hydrides are prepared by a variety of synthetic methods:

1. By direct action, a few covalent hydrides can be made by the direct reaction between the element and dihydrogen, e.g.

   $N_2 + 3H_2 \longrightarrow 3NH_3$ (Haber's process)

   $2H_2 + O_2 \longrightarrow 2H_2O$ (Spark-explosive)

   $H_2 + Cl_2 \longrightarrow 2HCl$ (Burn preparation of pure HCl)

   Elements which react with dihydrogen directly are 13 to 17 group elements.

2. By action of acids, on suitable binary compounds.

   $\underset{\text{Calcium phosphide}}{Ca_3P_2} + 3H_2SO_4 \longrightarrow 2PH_3 + 3CaSO_4$

   $\underset{\text{Ferrous sulphide}}{FeS} + H_2SO_4 \longrightarrow H_2S + FeSO_4$

   $\underset{\text{Magnesium nitride}}{2Mg_3N_2} + 6H_2SO_4 \longrightarrow 6MgSO_4 + 4NH_3$

   $\underset{\text{Aluminium carbide}}{Al_4C_3} + 12HCl \longrightarrow 3CH_4 + 4AlCl_3$

   $\underset{\text{Magnesium boride}}{3Mg_3B_2} + 4H_3PO_4 \longrightarrow \underset{\text{Tetraborane-10}}{B_4H_{10}} + 2\,Mg_3(PO_4)_2 + H_2$

3. By reduction of halide with lithium aluminium hydride, $LiAlH_4$ in a dry solvent such as ether.

   $4\,BCl_3 + 3LiAlH_4 \xrightarrow{\text{Ether}} \underset{\text{Diborane}}{2B_2H_6} + 3AlCl_3 + 3LiCl$

   $SiCl_4 + LiAlH_4 \xrightarrow{\text{Ether}} \underset{\text{Silane}}{SiH_4} + AlCl_3 + LiCl$

   $SnCl_4 + LiAlH_4 \xrightarrow{\text{Ether}} \underset{\text{Stannane}}{SnH_4} + LiCl + AlCl_3$

4. By reaction of an oxoacid with $NaBH_4$ in aqueous solution

   $4H_3AsO_4 + 3NaBH_4 \longrightarrow 4AsH_3 + 3H_3BO_3 + 3NaOH$

5. By converting one hydride into another by pyrolysis.

   $B_4H_{10} \xrightarrow{\Delta} B_2H_6 + \text{other products}$

Properties: Some of the important properties of covalent hydrides are as follows:

1. These hydrides consist of discrete covalent molecules held together by weak van der Waals forces and in some cases by hydrogen bonds. As a result, these hydrides are gases, liquids and in some cases solids having low melting and boiling points.
2. In general, these hydrides are volatile in nature and do not conduct electricity.
3. Hydrides of group 13 are electron deficient and hence behave as Lewis acids.

   $B_2H_6 + 2NH_3 \longrightarrow 2[H_3B \longleftarrow NH_3]$
4. Hydrides of group 15, 16 and 17 are electron rich and hence behave as Lewis bases.
5. The lighter elements of group 14, 15 and 16 form polynuclear hydrides in which two or more atoms of the same element are linked together. This property of self-linking of atoms is called catenation and carbon has maximum tendency for catenation.
6. Some hydrides act as reducing agents.

   $4AgNO_3 + SiH_4 \longrightarrow 4Ag + Si + 4HNO_3$

3.6.3 Metallic or Interstitial Hydrides

d-block elements of groups 3, 4, 5 (Sc, Ti, V, Y, Zr, Nb, La, Hf, Ta, Ac, etc.), 10, 11, 12 (Pb, Cu, Zn, etc) and *f*-block elements (Ce, Eu, Yb, Th, U etc.) on heating with H_2 under pressure form hydrides. In group 6, Cr atom forms the hydride, CrH.

The metals of groups 7, 8 and 9 do not form hydrides. In fact, the region of the periodic table from group 7 to 9 is referred to as the *hydride gap*.

These hydrides generally have properties similar to those of the parent metal and hence are known as *metallic hydrides*. Earlier,

it was thought that in these hydrides, hydrogen atom being small in size occupy some interstitial sites in the metal lattice thus producing distortion without any change in the metal itself. Hence, these hydrides are also known as *interstitial hydrides*. However, recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides have lattice different from the parent metal.

These hydrides are prepared by adsorbing hydrogen directly at appropriate temperatures by metal. The composition of these hydrides may not correspond to simple whole number ratio and therefore, they are known as *non-stoichiometric hydrides*. Their composition varies with temperature and pressure. This shows that hydrogen atoms occupy some and not all the interstitial sites in the metallic lattice. Thus the composition of the metallic hydrides is variable. Some important examples of metallic hydrides are ScH_2, YH_2, YH_3, LaH_2, LaH_3. Some examples of non-stoichiometric hydrides are $TiH_{1.5-1.8}$, $ZrH_{1.3-1.75}$, $VH_{0.56}$, $LaH_{2.87}$ etc.

Properties:

1. These hydrides have properties similar to those of metals, i.e. they are hard, conduct electricity, have metallic lustre and have magnetic properties.
2. Metallic hydrides are less dense than the metal from which they are prepared. This is because of crystal lattice expansion due to inclusion of H_2. Distortion of crystal structure makes the hydride brittle. Thus, when a metallic hydride is formed, solid piece of metal turns into finely powered hydride.
3. In many cases, the metallic hydrides formed are non-stoichiometric, e.g. $LaH_{2.87}$, $YbH_{2.55}$ etc. In such compounds law of constant composition does not hold good.
4. These interstitial hydrides may also be regarded as either alloys or interstitial solid solution of hydrogen in metals.
5. These hydrides on heating decompose and release hydrogen and a very finely divided metal and act as strong reducing agent. Finely divided metal can act as catalyst. The catalysts are thought to be effective by providing H atom rather than H_2 molecules. It is not certain whether the hydrogen is present in interstitial sites as atoms of hydrogen, or as $H^{\oplus}$ ions with delocalised electrons.
6. In interstitial hydride, metals have strong tendency to adsorb large volume of hydrogen on their surface. This property of adsorption of a gas by a metal is known as **occlusion.** The amount of hydrogen occluded is dependent on the nature and physical state of metal, i.e.

   Colloidal palladium > Palladium

   The Pd/ H_2 system is both extraordinary and interesting in the way, that when red hot Pd is cooled in H_2, it adsorbs or occludes about 935 times its own volume of H_2 or D_2 from He and other gases. But, on heating, the occluded hydrogen is liberated. Thus interstitial hydrides can be used as hydrogen storage media. This property has potential for hydrogen storage and as a source of energy for vehicles.

Besides the above-mentioned hydrides, three main categories of hydrides, i.e. ionic, covalent and metallic, some hydrides, better known as **polymeric hydrides** and **complex hydrides** are also f

a. **Polymeric hydrides:** These are formed by the elements having electronegativity in the range 1.4–2.0. They consist of monomer molecules held together in two or three dimensions by hydrogen bridges and thus are polymeric in nature. Some common examples are $(BeH_2)_n$, $(AlH_3)_n$, $(InH_3)_n$, $(SiH_4)_n$, etc. They are amorphous solids and stable up to 525 K. Above this temperature, they begin to evolve hydrogen gas.

b. **Complex hydrides:** These hydrides contain hydride ion ($H^{\ominus}$) coordinated to metal atoms/ions. These are formed by transition as well as non-transition elements. Group 13 elements are the most important non-transition elements, which form complex hydrides. Some common examples are $LiAlH_4$ (lithium aluminium hydride), $NaBH_4$ (sodium borohydride), etc. They are generally very good reducing agents.

3.7 WATER

Water is one of the most common, abundant and important substances known to man. Almost three-fourths of the earth's surface is covered with water. The distribution of water over the earth's surface is non-uniform. A major part of all living organisms is made up of water. Human body contains about 65% and some plants contain as much as 95% water. It is a very important compound for the survival of all living forms. It has great importance to a chemist because of its ability to dissolve large number of substances. Consequently, water serves as a medium, in which large number of chemical reaction occurs. It can be easily transformed from liquid to solid and to gaseous state. The term ice and steam are used to describe solid and gaseous state respectively.

Structure and aggregation of water molecules: In water molecule, the two H-atoms are bonded to O-atom by two covalent bonds [Fig. 3.3(a)]. The O-atom in H_2O is sp^3 hybridised. Each of the covalent bonds is formed by the axial overlap of $1s$-orbital of H-atom and sp^3 hybrid orbital of O-atom.

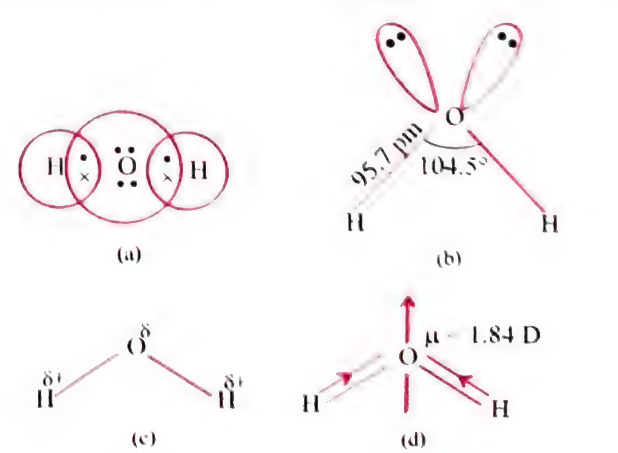


Fig. 3.3 (a) Lewis structure, (b) Structure of H_2O in gas phase, (c) Polar nature of water molecule and (d) Resultant dipole moment of water molecule

Since the O-atom in H_2O is sp^3 hybridized, the shape of H_2O molecule should be tetrahedral and ∠HOH bond angle should be

109.4°. But the H_2O water has been found to be a bent molecule with ∠HOH bond angle as 104.5°. This can be explained as follows:

According to Valence Shell Electron Pair Repulsion (VSEPR) theory,

Lone pair-lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion.

As a result, ∠HOH bond angle in H_2O gets reduced to 104.5°. In the gaseous state, H_2O exists as discrete molecule, as shown in Fig. 3.3(b).

Oxygen is more electronegative as compared to hydrogen (eletronegativity of O and H are 3.5 and 2.1 respectively). Hence the shared pair of electrons in O–H bond is shifted more towards O-atom, thereby partial negative charge (δ–) is developed on O-atom and partial positive charge (δ+) is developed on H-atom, hence H_2O is a polar molecule [Fig. 3.3(c)]. Since the two dipoles are inclined to each other at an angle of 104.5°, the bond moments of two O–H bond causes the molecule to behave as permanent electrical dipole. The dipole moment of water molecule [Fig. 3.3(d)] has been found to be 1.84 D and this confirms its polar nature.

In gaseous state, the individual covalent molecule of H_2O exists as such.

In liquid state, large aggregates of H_2O units are formed because of their association through intermolecular hydrogen bonds as shown in Fig. 3.4. The extent of association, however, depends upon the temperature and pressure.

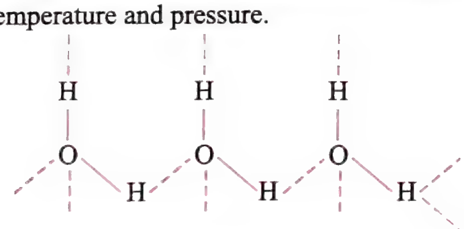
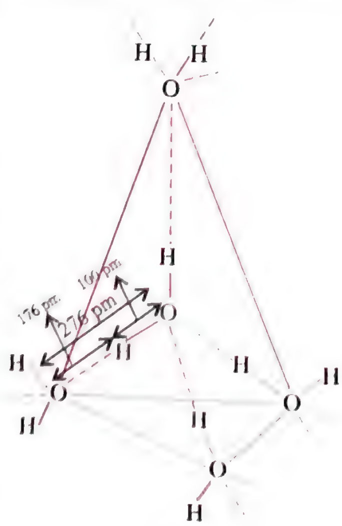


Fig. 3.4

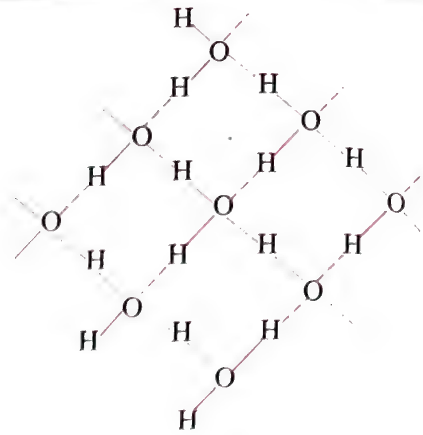
Experimental studies suggest that liquid water consists of aggregates of varying number of water molecules held together by intermolecular hydrogen bonds and free water molecule in dynamic equilibrium with the aggregates continuously forming, collapsing and reforming.

Solid state of water, i.e. ice is the crystalline form of water. In ice, each O-atom of H_2O molecule is covalently bonded (bond length 100 pm) to two H-atoms of its own molecules and with two H-atoms of the neighbouring H_2O molecules by H-bonds (bond length 76 pm). This type of bonding between O-atom and four H-atoms gives a tetrahedral structure to ice [Fig 3.5(a)].



(a)

Fig. 3.5 (a) Structure of tetrahedral unit in ice



(b)

Fig. 3.5 (b) Open cage structure of ice

This gives highly ordered three dimensional structure having vacant spaces, which may be compared to open cage and hence ice can be said to have open cage structure [Fig. 3.5(b)]. Open cage structure of ice can explain many of the properties of water which are as follows:

1. **Density of ice is less than water:** Open cage-like structure of ice has vacant space in it. The presence of vacant spaces gives a large volume to a given mass of ice. When the ice melts, some of the H-bonds in the cage-like structure of ice are broken to some extent and water molecules come closer to each other. This results in decrease in volume in the liquid state and increase in density. Thus, liquid water (at 0°C) has greater density than ice, this implies that ice is lighter than water.

2. **Ice floats on water:** Due to open-cage structure, ice has a relatively larger mass for a given mass of liquid water. Consequently, density of ice is less than water and ice floats on water.

3. **Density of water is maximum at 4°C or 277 K:** With the increase in temperature of liquid water at 273K (i.e. 0°C), density of water also increases. This is due to breaking of H-bonds causing aggregates of H_2O molecules to move together resulting in the decrease in volume thereby increase in density. This continues till 277 K (or 4°C). Above 277 K (i.e. 4°C), along with the breaking of H-bonds, kinetic energy of H_2O molecules also increases and hence H_2O molecules move away from each other, i.e. the volume increases. The increase in volume results in decrease in density. Thus, the density of water is maximum at 277 K (i.e. 4°C).

This property of maximum density of water at 277 K is a boon for the survival of aquatic animals during winter months because when the upper layer of the seawater freezes, the frozen water does not sink to bottom but keeps floating at the surface due to its lesser density. This provides thermal insulation to the water below it.

It is very interesting to note that nine different crystalline forms of ice have been found to exist under different present condition. Each one has different melting point. At one bar pressure ice has normal hexagonal form. However, at low temperature it adopts cubic form.

3.7.1 PROPERTIES OF WATER

3.7.1.1 Physical Properties

1. Water is colourless, tasteless and odourless.
2. It gives bluish tinge in thick layers.

The unusual properties of the water in the condensed phases (liquid and solid state) are due to the presence of extensive hydrogen bonding between water molecules. Some of the important physical properties are as follows:

1. The abnormally high freezing point, boiling point, heat of vapourisation and heat of fusion (compared to the hydrides of other elements of the same group of the periodic table, e.g. H_2S, H_2Te) are due to hydrogen bonding between H_2O molecule.
2. Water has a high specific heat, thermal conductivity and surface tension than most other liquids. These properties allow water to play a vital role in the biosphere. For example, the high heat of vapourisation and high heat capacity of water are responsible for moderation of the climate and body temperature of living organisms.
3. Water because of its high dielectric constant (78.38) has the ability to dissolve most of the inorganic (ionic) compounds and hence is regarded as universal solvent. Whereas, the ionic compounds are soluble due to ion-dipole interaction, covalent compounds such as alcohol amines, glucose, urea, sugar, etc. dissolve in water, due to the tendency of these molecules to form hydrogen bonds with water.
4. Water is an excellent solvent for transportation of ions and molecules needed for plant and animal metabolism.

3.7.1.2 Chemical Properties

1. **Stability:** Water is quite stable at ordinary temperatures, due to its high negative enthalpy of formation, $\Delta_f H^{\ominus} = -285.9\ \text{kJ mol}^{-1}$. But water decomposes into its elements at very high temperature.

$$2H_2O \rightleftharpoons 2H_2 + O_2 \qquad \Delta_f H = 486.2\ \text{kJ mol}^{-1}$$

However, the extent of decomposition is not very high. Water also decomposes into its constituent elements on passing electricity through it, in the presence of small amount of acid as alkali.

$$2H_2O_{(l)} \xrightarrow{\text{Electric current}} \underset{\text{(At cathode)}}{2H_{2(g)}} + \underset{\text{(At anode)}}{O_{2(g)}}$$

2. **Amphoteric character:** Water has the ability to behave both as an acid and a base, i.e. it behaves as an amphoteric substance.

Water is a weak electrolyte, i.e. it ionises to a little extent to give hydronium ion, $H_3O^{\oplus}$ and hydroxyl ion, $\overset{\ominus}{O}H$. Consequently, pure water has very low electrical conductivity.

$$\underset{\text{Acid}_1}{H_2O_{(l)}} + \underset{\text{Base}_2}{H_2O_{(l)}} \rightleftharpoons \underset{\text{Acid}_2}{H_3\overset{\oplus}{O}_{(aq)}} + \underset{\text{Base}_1}{\overset{\ominus}{O}H_{(aq)}}$$

$$K_w = 1 \times 10^{-14}\ \text{mol}^2\ \text{L}^{-2} \text{ at } 298\ \text{K}$$

In the Bronsted sense, water acts as an acid with NH_3 and a base with H_2S.

$$\underset{\text{Acid}_1}{H_2O_{(l)}} + \underset{\text{Base}_2}{NH_{3(aq)}} \rightleftharpoons \underset{\text{Acid}_2}{NH^{\oplus}_{4(aq)}} + \underset{\text{Base}_1}{\overset{\ominus}{O}H_{(aq)}}$$

$$\underset{\text{Acid}_1}{H_2O_{(l)}} + \underset{\text{Base}_2}{H_2S_{(aq)}} \longrightarrow \underset{\text{Acid}_2}{H_3O^{\oplus}_{(aq)}} + \underset{\text{Base}_1}{HS^{\ominus}_{(aq)}}$$

In general, water can behave as an acid towards bases stronger than it and as a base towards acids stronger than it.

The auto-protolysis, i.e. self-ionisation may be represented as

$$\underset{\substack{\text{Acid}_1\\ \text{(acid)}}}{H_2O_{(l)}} + \underset{\substack{\text{Base}_2\\ \text{(base)}}}{NH_{3(aq)}} \rightleftharpoons \underset{\substack{\text{Acid}_2\\ \text{(conjugate}\\ \text{acid)}}}{NH^{\oplus}_{4(aq)}} + \underset{\substack{\text{Base}_1\\ \text{(conjugate}\\ \text{base)}}}{\overset{\ominus}{O}H_{(aq)}}$$

3. **Redox reaction:** Water behaves both as an oxidising agent and a reducing agent.

a. **As an oxidising agent:** Water reacts with a number of active metals, whose electrode potential is less than – 0.83 V, thus liberating H_2 gas.

$$2H_2O_{(l)} + 2e^{\ominus} \longrightarrow 2\overset{\ominus}{O}H + H_{2(g)}; \qquad E^{\ominus} = -0.83\ \text{V}$$

$$\underset{\substack{\text{Reducing}\\ \text{agent}\\ \text{or}\\ \text{redutcant}}}{2Na_{(s)}} + \underset{\substack{\text{Oxidising}\\ \text{agent}\\ \text{or}\\ \text{oxidant}}}{2H_2O_{(l)}} \longrightarrow 2NaOH + H_{2(g)}$$

$$Ca_{(s)} + 2H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)} + H_{2(g)}$$

It is decomposed by metals such as Zn, Mg, Fe, etc., when steam is passed over hot metals.

$$Zn + H_2O \longrightarrow ZnO + H_2$$

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$$

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

Pb and Cu decompose water only at a white heat. Ag, Au, Hg and Pt metals do not decompose water.

When steam is passed over red hot coke (1000°C), water gas is formed.

$$C + H_2O \longrightarrow \underbrace{CO + H_2}_{\text{Water gas}}$$

In all these reactions, water act as an oxidising agent and itself gets reduced to dihydrogen gas.

b. **As a reducing agent:** Water reacts with highly electronegative elements like fluorine, whose electrode potential is higher than +1.23 V, thus liberating dioxygen and trioxygen.

$$O_{2(g)} + 4H^{\oplus}_{(aq)} + 4e^{\ominus} \longrightarrow 2H_2O_{(l)} \qquad E^{\ominus} = +1.23\ \text{V}$$

$$2F_{2(g)} + 2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^{\oplus}_{(aq)} + 4F^{\ominus}_{(aq)}$$

or

$$2F_2 + 2H_2O \longrightarrow O_2 + 2H_2F_2$$

$$3F_{2(g)} + 3H_2O_{(l)} \longrightarrow O_{3(g)} + 6F^{\ominus}_{(aq)} + 6H^{\oplus}_{(aq)}$$

In the above reactions, H_2O behaves as a reducing agent and itself gets oxidised to O_2 or O_3.

4. **Hydrolytic reaction:** Water with a high dielectric constant has a strong solvating character. It acts as an excellent solvent. Because of the great affinity for oxygen, hydrolysis of ionic as well as covalent compound occurs in water. In these reactions, $H^{\oplus}$ and $\overset{\ominus}{O}H$ ions of water interact with the anions and cations of the compound respectively, leading to the formation of an acid or base or both. Water can hydrolyse:

   a. **Metallic oxides:** Metallic or basic oxides react with water to form alkalis.

   $$Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$$
   $$CaO_{(s)} + H_2O \longrightarrow Ca(OH)_{2(aq)}$$

   b. **Non-metallic oxides:** Non-metallic or basic oxides react with water to form acids.

   $$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons \underset{\text{Carbonic acid}}{H_2CO_{3(aq)}}$$
   $$N_2O_5 + H_2O \longrightarrow \underset{\text{Nitric acid}}{2HNO_3}$$
   $$P_4O_{10(s)} + 3H_2O_{(l)} \longrightarrow \underset{\text{Phosphoric acid}}{4H_3PO_{4(aq)}}$$
   $$SO_{2(aq)} + H_2O_{(l)} \longrightarrow \underset{\text{Sulphurous acid}}{H_2SO_{3(aq)}}$$
   $$SO_{3(g)} + H_2O_{(l)} \longrightarrow \underset{\text{Sulphuric acid}}{H_2SO_{4(aq)}}$$
   $$Cl_2O_{7(g)} + H_2O_{(l)} \longrightarrow \underset{\text{Perchloric acid}}{2HClO_{4(aq)}}$$

   c. **Hydrides:** Water decomposes hydrides to liberate dihydrogen gas, e.g.

   $$CaH_{2(s)} + 2H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)} + 2H_{2(g)}$$

   d. **Carbides:** Water decomposes carbides to liberate methane or acetylene, e.g.

   $$Al_4C_{3(s)} + 12H_2O_{(l)} \longrightarrow 4Al(OH)_{3(aq)} + \underset{\text{Methane}}{3CH_{4(g)}}$$
   $$CaC_{2(s)} + 2H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)} + \underset{\text{Acetylene}}{C_2H_{2(g)}}$$

   e. **Nitrides:** Water decomposes nitrides to liberate ammonia (NH_3), e.g.

   $$Mg_3N_{2(s)} + 6H_2O_{(l)} \longrightarrow 3Mg(OH)_{2(aq)} + 2NH_{3(g)}$$
   $$AlN_{(s)} + 3H_2O \longrightarrow Al(OH)_{3(aq)} + NH_{3(g)}$$
   $$Ca_3N_{2(s)} + 6H_2O_{(l)} \longrightarrow 3Ca(OH)_{2(aq)} + 2NH_{3(g)}$$

   f. **Phosphides:** Water decomposes phosphides to liberate phosphine $(PH)_3$, e.g.

   $$\underset{\text{Calcium phosphide}}{Ca_3P_{2(s)}} + 6H_2O_{(l)} \longrightarrow 3Ca(OH)_{2(aq)} + \underset{\text{Phosphine}}{2PH_{3(g)}}$$

   g. **Salts:**

   $$AlCl_{3(s)} + 6H_2O_{(l)} \longrightarrow [Al(H_2O)_6]^{3+}_{(aq)} + 3Cl^{\ominus}_{(aq)}$$
   $$Na_2CO_{3(s)} + 2H_2O \longrightarrow 2NaOH + H_2CO_{3(aq)}$$

   Hydrolysis of Na_2CO_3(sodium carbonate) produces strong base, NaOH and weak acid, H_2CO_3. Hence aqueous solution of Na_2CO_3 is alkaline in nature.

   $$CuSO_{4(s)} + 2H_2O_{(l)} \rightleftharpoons Cu(OH)_2(aq) + H_2SO_{4(aq)}$$

   Hydrolysis of $CuSO_4$ produces a weak base $Cu(OH)_2$ and strong acid, H_2SO_4, hence aqueous solution of $CuSO_4$ is acidic is nature.

5. **Hydrate formation:** Water combines with many salts during crystallisation to form hydrates, for example $CuSO_4{\cdot}5H_2O$. The water present in the hydrates is called water of crystallisation and the salts are called hydrated salts or simply hydrates. There are three main type of hydrates:

   a. **Coordinated water:** Water molecules are coordinated to the central metal ion to form complex ion, e.g.

   $[Ni\,(OH_2)_6]^{2+}\,(NO_3^{\ominus})_2$

   $[Fe\,(OH_2)_6]^{3+}\cdot 3Cl^{\ominus}$

   $[Cr\,(OH_2)_6]^{3+}\cdot 3Cl^{\ominus}$

   b. **Hydrogen bonded water:** Compounds in which water molecule may be hydrogen bonded to oxygen containing anions, e.g. in $CuSO_4{\cdot}5H_2O$, four H_2O molecules are present as coordinate water as they form coordinate bond with central Cu^{2+} ion and the fifth water molecule is linked to sulphate ion, SO_4^{2-} by hydrogen bond. Hence $CuSO_4{\cdot}5H_2O$ may be represented as $[Cu(H_2O)_4]^{2+}$ $SO_4^{2-}\cdot H_2O$.

   Similarly, $FeSO_4{\cdot}7H_2O$ (green vitriol), $ZnSO_4{\cdot}5H_2O$ (white vitriol) may be represented as

   $[Fe(H_2O)_6]^{2+}\,SO_4^{2-}\cdot H_2O$ and $[Zn(H_2O)_4]^{2+}\,SO_4^{2-}\cdot H_2O$

   c. **Interstitial water:** Water molecule(s) is (are) present in certain compounds as interstitial water i.e. it occupies interstitial sites or intersticies. For example in $BaCl_2{\cdot}2H_2O$, the two water molecules occupy the voids in the crystal lattice.

6. **As a catalyst:** Perfectly dry gases generally do not react but the presence of moisture brings the chemical change. Ammonia (NH_3) and hydrochloric gas (HCl) combine only in the presence of water, and hence water acts as a catalyst in such reactions.

7. **Tests of H_2O:**

   a. A drop of water when added to anhydrous copper sulphate changes its colour from white to blue, due to formation of hydrated copper sulphate, $CuSO_4{\cdot}5H_2O$ which is blue in colour.

   $$\underset{\text{Anhydrous}}{CuSO_{4(s)}} + 5H_2O \longrightarrow \underset{\text{Blue}}{CuSO_4{\cdot}5H_2O}$$

   b. Water reacts with calcium carbide, CaC_2, SrC_2 and BaC_2 to evolve acetylene which burns with bright flame.

   $$\underset{\text{Calcium carbide}}{CaC_2} + H_2O \longrightarrow Ca(OH)_{2(s)} + \underset{\text{Acetylene}}{HC \equiv CH_{(g)}}$$

Whereas water with Be_2C and Al_4C_3 gives CH_4 gas and with Mg_2C_3 gives propyne gas.

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_{2(s)} + CH_{4(g)}$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_{3(s)} + 3CH_{4(g)}$$

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3-C\equiv CH_{(g)}$$

3.7.2 HARD AND SOFT WATER

Water which produces lather with soap is called *soft water* and which does not produce lather with soap is called *hard water*.

Hardness is due to the presence of bicarbonate, chlorides, and sulphates of Ca and Mg.

$$M^{2+} + 2C_{17}H_{35}COONa \longrightarrow (C_{17}H_{35}COO)_2M + 2Na^{\oplus}$$

$(M = Ca^{2+}, Mg^{2+})$ Sodium stearate (soap)

Ca^{2+} or Mg^{2+} ions present in hard water react with soap to form a precipitate of Ca and Mg salts of fatty acids and hence no lather is produced.

3.7.2.1 Type of Hardness

Temporary hardness or *carbonate hardness* is due to the presence of soluble $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ and *permanent or non-carbonate hardness* is due to the presence of $CaCl_2$, $MgCl_2$, $CaSO_4$ and $MgSO_4$. The process of removal of Ca^{2+} or Mg^{2+} ion is called softening of water.

3.7.2.2 Removal of Hardness of Water

Removal of temporary hardness:

1. **By boiling:**

$$\underset{(M = Ca \text{ or } Mg)}{M(HCO_3)_2} \longrightarrow \underset{\text{Insoluble, settles down}}{MCO_3\downarrow} + H_2O + CO_2$$

2. **Clark's method:**

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow \underset{\text{Insoluble}}{2CaCO_3\downarrow} + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow \underbrace{MgCO_3\downarrow + CaCO_3\downarrow}_{\text{Insoluble}} + H_2O$$

Removal of permanent hardness:

1. **By washing soda:** $(Na_2CO_3 \cdot 10H_2O)$

$$M^{2+} + CO_3^{2-} \longrightarrow MCO_3$$

2. **Ion exchange method (Inorganic cation exchangers; Fig. 3.6; permutit method):** Permutit is an artificial zeolite, chemically it is sodium aluminium ortho silicates. $Na_2Al_2Si_2O_8 \cdot xH_2O$ or $(NaAlSiO_4 \cdot 3H_2O)$

$$2NaAlSiO_4 + Ca^{2+} \longrightarrow (AlSiO_4)_2Ca + 2Na^{\oplus}$$

or

$$\underset{\text{Sodium zeolite}}{Na_2Z} + \underset{(Ca^{2+} \text{ or } Mg^{2+})}{MCl_2} \longrightarrow \underset{\text{(Calcium or magnesium zeolite)}}{MZ + 2NaCl}$$

$[Z = Al_2Si_2O_8 \cdot xH_2O]$

The exhausted resin is regenerated by passing 10% solution of NaCl.

$$\underset{\text{Exhausted resin}}{MZ} + 2NaCl \longrightarrow \underset{\text{Regenerated resin}}{Na_2Z} + MCl_2$$

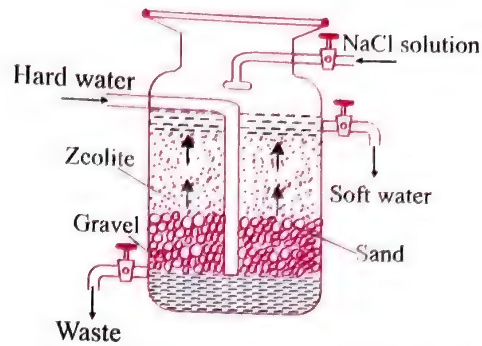


Fig. 3.6 Permutit method for water softening

3. **Organic ion exchanger (Fig. 3.7):** These are complex organic molecules having big molecules with either acidic group (—SO_3H or —COOH) or basic group ($\overset{\ominus}{O}H$ or $\overset{\ominus}{N}H_2$) attached to them. Cation exchangers are capable of exchanging $H^{\oplus}$ ions for cations and are represented by $H^{\oplus}$-resin, whereas the anion exchangers are capable of exchanging $\overset{\ominus}{O}H$ or $\overset{\ominus}{N}H_2$ ions for other anions and are represented as $\overset{\ominus}{O}H$-resin.

Reactions in cation exchanger:

$$\underset{(Ca^{2+} \text{ or } Mg^{2+})}{M^{2+}} + 2(H^{\oplus}\text{-resin}) \longrightarrow M(\text{resin})_2 + 2H^{\oplus}$$

Reactions in anion exchanger:

$$Cl^{\ominus} + (\overset{\ominus}{O}H\text{-resin}) \longrightarrow (Cl^{\ominus}\text{-resin}) + \overset{\ominus}{O}H$$

$$SO_4^{2-} + 2(\overset{\ominus}{O}H\text{-resin}) \longrightarrow [SO_4^{2-}(\text{resin})_2] + 2\overset{\ominus}{O}H$$

$$2H^{\oplus} + 2\overset{\ominus}{O}H \longrightarrow 2H_2O$$

The water obtained by this method is free from all types of cations and anions and known as deionised or demineralised water.

Regeneration of resins:

$$\underset{\text{Exhausted resin}}{Ca(\text{resin})_2} + 2HCl \longrightarrow CaCl_2 + \underset{\text{Regenerated resin}}{2(H^{\oplus}\text{-resin})}$$

$$(Cl^{\ominus}\text{-resin}) + NaOH \longrightarrow NaCl + \underset{\text{Regenerated resin}}{(\overset{\ominus}{O}H\text{-resin})}$$

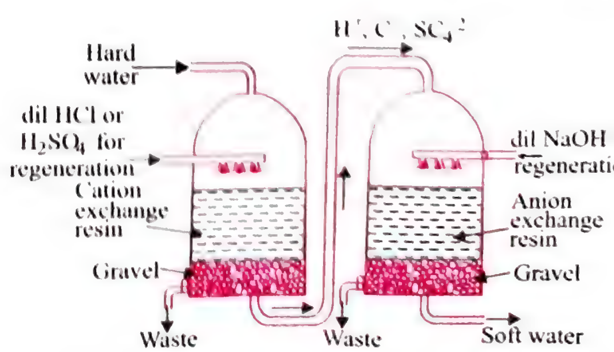


Fig. 3.7. Ion exchange process involving organic resins

3.7.2.3 Internal Treatment of Hardness by Calgon Process (Sequestration)

In this process, Ca^{2+} and Mg^{2+} ions present in hard water are rendered ineffective (sequestrated) by treatment with sodium polymetaphosphate $(NaPO_3)_x$, where x is as high as 100, or more commonly with sodium hexametaphosphate $(NaPO_3)_6$ or $Na_2[Na_4(PO_3)_6]$. Its trade name is calgon (which means calcium gone.)

When calgon is added to hard water, the Ca^{2+} and Mg^{2+} ions present in it combine with $(NaPO_3)_6$ to form a soluble complex of Ca and Mg salts.

$$\underset{\substack{(M = Ca \text{ or } Mg)\\ (\text{From hard water})}}{2MCl_2} + Na_2[Na_4(PO_3)_6] \longrightarrow \underset{\substack{(M = Ca \text{ or } Mg)\\ (\text{Complex salt soluble})}}{Na_2[M_2(PO_3)_6]} + 4NaCl$$

The complex Ca and Mg ions do not form any precipitate with soap and hence readily produce lather with soap solution.

Hard water is unsuitable for laundry, washing and dyeing. It is also harmful for steam boilers. Over a period of time the inner surface of the boiler gets crusted with the so called **"boiler scale"** which is largely $CaSO_4$, $CaCO_3$ and MgOCl (magnesium oxychloride). The deposition reduces the efficiency of the boiler and also damages it. It is therefore necessary to render the water soft before it can be used.

3.7.2.4 Units and Degree of Hardness of Water in Terms of parts per million (ppm)

Concentration of solute (in ppm) = mass of solute in gram in 10^6 mL solution. It is used in determining the *hardness of water* due to the presence of bicarbonates (temporary hardness), chlorides and sulphates (permanent hardness) of calcium and magnesium.

The degree of hardness is defined as the number of parts of $CaCO_3$ or equivalent to other Ca and Mg salts present in a million (10^6) parts of water.

$$\text{EW } (CaCO_3) = \frac{100}{2} = 50; \text{ EW } (MgSO_4) = \frac{120}{2} = 60$$

$$\text{EW } (CaCl_2) = \frac{111}{2} = 55.5$$

This means 50 g of $CaCO_3 \equiv$ 60 g of $MgSO_4$

$\equiv$ 55.5 g of $CaCl_2$

Examples:

1. Degree of hardness in a water sample containing 222 ppm of $CaCl_2$

   55.5 g $CaCl_2 \equiv$ 50 g of $CaCO_3$

   $$222 \text{ g } CaCl_2 \equiv \frac{50 \times 222}{55.5} = 200 \text{ ppm}$$

2. Degree of hardness in a water sample containing 36 mg of $MgSO_4$ per kg of water

   10^3 mL or 10^3 g H_2O contains $MgSO_4$ = 36 mg

   10^6 g H_2O contains $MgSO_4 = 36 \times 10^3$ mg = 36 g

   From the formula

   1 mol of $MgSO_4 \equiv$ 1 mol of $CaCO_3$

   120 g of $MgSO_4 \equiv$ 100 g of $CaCO_3$

   $$36 \text{ g of } MgSO_4 = \frac{100 \times 36}{120} = 30 \text{ g of } CaCO_3$$

   $\therefore$ Degree of hardness = 30 ppm

Hardness in terms of $CaCO_3$ equivalents

The reason of expressing hardness as $CaCO_3$ equivalents is due to the fact that its molecular mass is 40 + 12 + 48 = 100 (or equivalent weight = 50) and it is the most insoluble salt that can be precipitated in water treatment.

Equivalent of $CaCO_3$

$$= \frac{\text{Mass of hardness producing substance} \times \text{Chemical equivalent of } CaCO_3}{\text{Chemical equivalent of hardness producing substance}}$$

$$= \frac{\text{Mass of hardness producing substance} \times 50}{\text{Chemical equivalent of hardness producing substance}}$$

For example, the molecular mass of $Ca(HCO_3)_2$ is 162 and that of $CaCO_3$ is 100. So, $CaCO_3$:$Ca(HCO_3)_2$ = 100 : 162. The chemical equivalent of $Ca(HCO_3)_2$ is 162/2 = 81. In other words, 162 parts by mass of $Ca(HCO_3)_2$ or 2 equivalent react with same amounts as 100 parts by mass of $CaCO_3$ of 2 equivalent. The $Ca(HCO_3)_2$ expressed as $CaCO_3$ equivalent can be written as:

$$162 \times \frac{100}{162} = 100 \text{ equivalent of } CaCO_3 \text{ factor}$$

Similarly,

$CaSO_4$:$CaCO_3$	=	136:100	100/136
$CaCl_2$:$CaCO_3$	=	111:100	100/111
$MgCl_2$:$CaCO_3$	=	95:100	100/95
$MgSO_4$:$CaCO_3$	=	120:100	100/120
$MgCO_3$:$CaCO_3$	=	84:100	100/84

It should be noted that chemical equivalents of $CaCO_3$, $CaSO_4$, $CaCl_2$, $MgCl_2$, $MgSO_4$ and $MgCO_3$, are 50, 68, 55.5, 47.5, 60 and 42, respectively.

$$1 \text{ ppm} = \frac{1 \text{ part of hardness}}{10^6 \text{ parts of water}}$$

ILLUSTRATION 3.6

A sample of hard water contains 1 mg $CaCl_2$ and 1 mg $MgCl_2$ per litre. Calculate the hardness of water in terms of $CaCO_3$ present in per 10^6 parts of water.

a. 2.5 ppm **b.** 1.95 ppm **c.** 2.15 ppm **d.** 195 ppm

Sol.

b. Molecular weight of $CaCl_2$ = 111.0 g

MW of $CaCO_3$ = 100 g

MW of $MgCl_2$ = 95.0 g

$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$

$MgCl_2 + Na_2CO_3 \longrightarrow MgCO_3 + 2NaCl$

i. $111.0 \text{ g } CaCl_2 \equiv 100 \text{ g } CaCO_3$

$1 \text{ mg } CaCl_2 \equiv \frac{100}{111} \text{ mg } CaCO_3 = 0.9 \text{ mg } CaCO_3$

ii. $95.0 \text{ g } MgCl_2 \equiv 100 \text{ g } CaCO_3$

$1 \text{ mg } MgCl_2 \equiv \frac{100}{95} \text{ mg } CaCO_3 = 1.05 \text{ mg } CaCO_3$

Hardness of $CaCO_3$ ppm

$$\equiv \frac{(0.9 + 1.05) \times 10^{-3} \text{g} \times 10^6 \text{mL}}{10^3 \text{ mL}}$$

$= 1.95$ ppm

ILLUSTRATION 3.7

A water sample is found to contain 96 ppm of SO_4^{2-} and 122 ppm of $HCO_3^{\ominus}$ with Ca^{2+} ion as the only cation.

a. Calculate the ppm of Ca^{2+} in water.
b. Calculate the mol of CaO required to remove $HCO_3^{\ominus}$ ion from 1000 kg of the water.
c. Calculate the concentration of Ca^{2+} in ppm remaining in water after adding CaO.

Sol.

a. $CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$ ...(i)

$Ca(HCO_3)_2 \rightleftharpoons Ca^{2+} + 2HCO_3^{\ominus}$ ...(ii)

i. 96 ppm of $SO_4^{2-} = 96 \text{ g } SO_4^{2-}$ in 10^6 mL H_2O

(MW of $SO_4^{2-} = 96$ g)

$= \frac{96}{96}$ mol of $SO_4^{2-}/10^6$ mL H_2O

$= 1$ mol of $SO_4^{2-}/10^6$ mL H_2O

$= 1$ mol of $Ca^{2+}/10^6$ mL H_2O

ii. 122 ppm of $HCO_3^{\ominus} \equiv 122 \text{ g } HCO_3^{\ominus}$ in 10^6 mL H_2O

(MW of $HCO_3^{\ominus} = 61$ g)

$\equiv \frac{122}{61} = 2$ mol of $HCO_3^{\ominus}$

$\equiv 1.0$ mol of Ca^{2+}

[Since 1 mol of $Ca(HCO_3)_2 = 2$ mol of $HCO_3^{\ominus}$]

Total $Ca^{2+} = 1 + 1 = 2$ mol of $Ca^{2+} = 80$ g in 10^6 mL H_2O

$\boxed{\text{ppm } Ca^{2+} = 80}$

b. $\underset{1 \text{ mol}}{CaO} + \underset{1 \text{ mol}}{Ca(HCO_3)_2} \longrightarrow \underset{2 \text{ mol}}{2CaCO_3} + H_2O$ ...(iii)

$= 2$ mol $HCO_3^{\ominus}$ in 10^6 g H_2O

2 mol of $HCO_3^{\ominus}$ is present in 10^6 mL ($= 10^6$ g) $= 1000$ kg of H_2O.

From Eq. (iii), 1 mol of CaO is required to remove 2 mol of $HCO_3^{\ominus}$ present in 1000 kg of H_2O.

c. Total Ca^{2+} already present $= 2$ mol

Ca^{2+} removed in Eq. (iii) $= 1$ mol

Thus Ca^{2+} (left) $= 2 - 1 = 1$ mol $= 40$ g $= 40$ ppm

From Eq. (iii), it is clear that $HCO_3^{\ominus}$ ions are removed as $CaCO_3$, but SO_4^{2-} ions are left in the solution.

ILLUSTRATION 3.8

Hardness of water is 200 ppm. The normality and molarity of $CaCO_3$ in the water is

a. 2×10^{-6} N, 2×10^{-6} M
b. 4×10^{-2} N, 2×10^{-2} M
c. 4×10^{-3} N, 2×10^{-3} M
d. 4×10^{-1} N, 2×10^{-1} M

Sol.

c. Hardness is weight in grams of $CaCO_3$ in 10^6 mL of H_2O or $= 10^6$ g of H_2O ($\because d\,H_2O = 1$)

MW ($CaCO_3$) $= 100 \text{ g mol}^{-1}$

$$M = \frac{W_2 \times 1000}{\text{MW} \times \text{Volume of solution in mL}}$$

$$= \frac{200 \times 1000}{100 \times 10^6} = 2 \times 10^{-3} \text{ M}$$

$N = n \times M = 2 \times 2 \times 10^{-3} = 4 \times 10^{-3}$ N

Hence, the correct option is (c).

ILLUSTRATION 3.9

A sample of hard water contains 122 ppm of $HCO_3^{\ominus}$ ions. What is the minimum weight of CaO required to remove ions completely from 1 kg of such water sample?

a. 56 mg
b. 112 mg
c. 168 mg
d. 244 mg

Sol.

a. [MW ($HCO_3^{\ominus}$) $= 61$ g, MW (CaO) $= 56$ g]

Temporary hardness is due to the $HCO_3^{\ominus}$ of Ca^{2+} and Mg^{2+} and is removed by either boiling or by treating with CaO or $Ca(OH)_2$ (Clark's method).

$\underset{1 \text{ mmol}}{Ca(HCO_3)_2} + \underset{1 \text{ mmol}}{CaO} \longrightarrow \underset{2 \text{ mmol}}{2CaCO_3} + H_2O$ ...(i)

122 ppm of $HCO_3^{\ominus} \equiv 122 \text{ g } HCO_3^{\ominus}$ in 10^6 mL or 10^3L

$\equiv 122 \text{ mg } HCO_3^{\ominus}$ in 1.0 L

$\equiv \frac{122}{61} = 2$ mmol in 1.0 L

According to Eq. (i),

2 mmol of $Ca(HCO_3)_2 \equiv 2$ mmol of CaO in 1.0 L

1 mmol of $Ca(HCO_3)_2 \equiv 1$ mmol of CaO in 1.0 L

$\equiv 1 \times 56 \equiv 56$ mg of CaO

$\equiv 56$ mg of CaO in 1.0 L

$\equiv 56$ mg of CaO in 1 kg of H_2O

(1 L of $H_2O \equiv 1$ kg of H_2O, $\because d\,H_2O = 1$)

Hence, the correct option is (a).

ILLUSTRATION 3.10

100 mL samples of distilled water, tap water and boiled water required, respectively, 2 mL, 17 mL and 7 mL of soap solution to form permanent lather. The ratio of permanent to temporary hardness in the tap water is

a. 3:2 **b.** 2:3 **c.** 1:2 **d.** 2:1

Sol. c.

	Distilled H_2O (No hardness, lather factor)	Tap H_2O (Temporary + permanent hardness)	Boiled H_2O (Only permanent hardness; temporary hardness is removed by boiling)
Volume of soap solution required	2 mL	17 mL	7 mL
Volume of soap effectively used	–	17 – 2 = 15 mL	7 – 2 = 5 mL

(Temporary and permanent hardness) in tap H_2O = 15 mL

Permanent hardenss in boiled H_2O = 5 mL

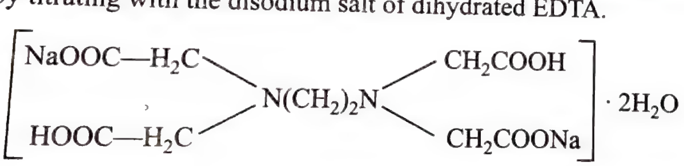
Temporary hardness in H_2O = 15 – 5 = 10 mL

$$\frac{\text{Permanent hardness}}{\text{Temporary hardness}} = \frac{5}{10} = 1:2$$

Hence, answer is (c).

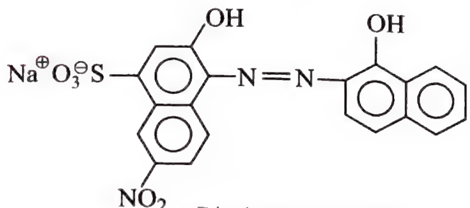
3.7.2.5 Estimation of Mg^{2+} and Ca^{2+} Ions by EDTA Titration

Mg^{2+} and Ca^{2+} ions can be detected and estimated in hard water by titrating with the disodium salt of dihydrated EDTA.



(MW = 372.25 g mol^{-1}) at pH = 10 using ($NH_4OH + NH_4Cl$) buffer using azo dye called *eriochrome black-T* or *solochrome black* indicator. The end point is given by change in colour from wine red to pure blue. Since the action of the indicator and formation of metal EDTA complex is governed by pH, pH of the solution is kept constant by adding suitable buffer.

Eriochrome black-T: It is sodium (1-hydroxy-2-naphthylazo)-6-nitro-2-napthol-4-sulphonate. It is also known as solochrome black or WDFA. In strong acidic solution, eriochrome black-T (EBT) polymerises to a red-brown product and metal complexes usually red in colour. It is a triprotic acid and represented as H_3In. The proton of sulphonic acid group remains ionised in aqueous solution regardless of pH and thus the ion shown is $H_2In^{\ominus}$ which is red in colour.



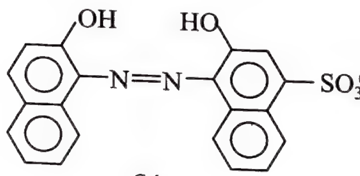
Eriocrhome Black-T (EBT)

$$\underset{\text{Red}}{H_2In^{\ominus}} \xrightleftharpoons{\text{pH5.5–7.0}} \underset{\text{Blue}}{HIn^{2-}} \xrightleftharpoons{\text{pH7–11}} \underset{\text{Yellowish orange}}{In^{3-}}$$

The colour at different pH given by EBT are:
Below pH 5.5 —Red
Between pH range 7–11—Blue
Above pH 11.5—Yellowish orange

pH range 7–11, when metallic salts are added, the colour of the indicator changes from blue to red. At the end point in EDTA titration, the indicator will be set free and colour change will be from wine *red to blue.*

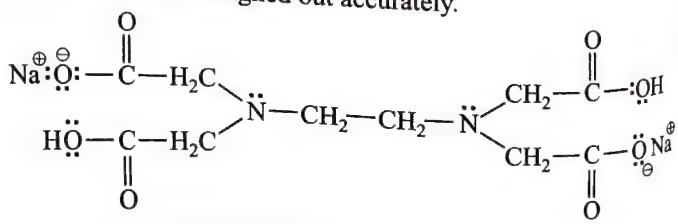
Solochrome dark blue or calcon: This is also sometimes called *eriochrome blue black-R*. It is sodium-1-(2-hydroxy-l-naphthylazo)-2-naphthol-4-sulphonate. This has two ionisable phenolic hydrogen atoms with stepwise *pKa* values of 7.4 and 13.5, respectively. *This is also used as an indicator in EDTA titration of Ca^{2+} ions in the presence of Mg^{2+} ions.* This is suitable only at pH = 12.3 (obtained with diethylamine buffer: 5 mL 1000 mL^{-1} of solution) in order to avoid the interference of Mg^{2+} ions. The colour change is from *pink to pure blue.*



Calcon

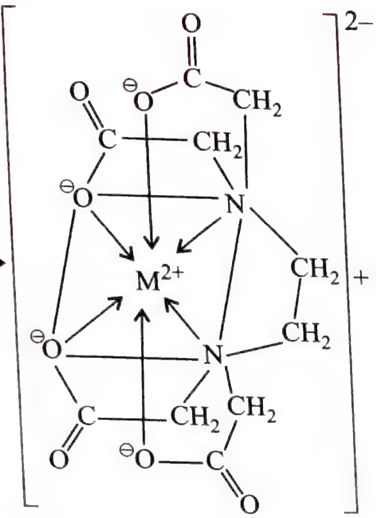
Standard EDTA solution: Disodium dihydrogen ethylene diamine tetra acetate dihydrate is used as a primary standard. However, many samples contain moisture, which is difficult to remove through drying. In such cases, the solution is standardised against standard zinc or magnesium solution.

The molecular weight of dihydrate salt is 372.25 and after drying at 80°C, it can be weighed out accurately.



Disodium salt of EDTA (Na_2H_2EDTA)
[Complexation of EDTA with Ca^{2+} and Mg^{2+} ions]

$[H_2EDTA]^{2-} + M^{2+} \longrightarrow$
$(M^{2+} = Ca^{2+}$ and $Mg^{2+})$



$+ 2H^{\oplus}$

For simplicity, it is represented as

$H_2Y^{2-} + M^{2+} \longrightarrow MY^{2-} + 2H^{\oplus}$

3.7.2.6 Determination of Ca^{2+} and Mg^{2+} present together in hard water

A solution having both Ca^{2+} and Mg^{2+} ions in the sample is titrated using eriochrome black-T (solochrome black-T) indicator with EDTA solution at pH = 10, and this titre value gives the total Ca^{2+} and Mg^{2+} ions present in the sample. The pH = 10 is maintained by adding buffer solution of NH_4Cl and NH_4OH.

The colour of the solution changes from wine red to blue at the end point.

1 mL of 0.1 M EDTA = 2.4 mg of Mg
1 mL of 0.1 M EDTA = 0.4 mg of Ca

3.7.2.7 Determination of Ca^{2+} and Mg^{2+} ions separately in hard water

In an equal amount of sample containing Ca^{2+} and Mg^{2+} ions, calcon or HHSNNA is used as an indicator and titrated with EDTA, which gives the titre value of Ca^{2+} ions in the presence of Mg^{2+} ions. The Mg^{2+} ions are precipitated as $Mg(OH)_2$ by adding suitable amount of NaOH or KOH. The solution after precipitation of Mg^{2+} ions as $Mg(OH)_2$ is stirred and then titrated with standard EDTA untill the colour changes from *pink to blue* (in case of calcon) and from *wine red to purplish blue* (in case of HHSNNA) indicator.

For example, let the volume of 0.1 M EDTA in the determination of both Ca^{2+} and Mg^{2+} ions be X mL and with Ca^{2+} ions only (using *calcon* indicator) be Y mL.

Now subtract the EDTA volume required for the Ca^{2+} ions only from the volume required for the total Ca^{2+} and Mg^{2+} ions. The difference of volume of EDTA is equivalent to Mg^{2+} ions in the mixture. Then, mg of $Ca^{2+} = 0.4 \times Y$ and mg of $Mg^{2+} = (X - Y) \times 2.4$.

Second method for the determination of Ca^{2+} ion present in hard water using calcon as indicator

The solution having Ca^{2+} ion is titrated using calcon indicator with EDTA at higher pH = 12, by using 2 mL of 1 M NaOH or KOH. The colour change at the end point is from **pink to pure blue.** 1 mL of 0.1 M EDTA = 0.4 mg of Ca.

3.7.2.8 Determination of the total hardness of water

EDTA is used as a complexing reagent and it forms soluble complexes with Ca^{2+} and Mg^{2+}. End point is detected by colour change of the indicator eriochrome black-T. The stability of the complex and colour change of the indicator depend on the pH of the titrating medium. Hence, the solution must be well buffered by $(NH_4OH + NH_4Cl)$ buffer solution of pH = 10. At the end point, the concentration of metal ion decreases abruptly.

A metal ion indicator forms a complex with a metal ion:

$M^{2+} + HIn^{2-} \longrightarrow MIn^{\ominus} + H^{\oplus}$

where HIn^{2-} shows indicator form at a particular pH.

However, metal ion indicator complexes are usually less stable than the metal EDTA complexes. The indicator releases the metal ions at the end point, and this shows a colour change. In this titration, in the presence of metal ions, eriochrome black-T forms a wine red complex. At the end point when the metal ions are completely complexed with EDTA, the *colour changes to blue* (of the free indicator).

$$\underset{\text{Wine red}}{MIn^{\ominus}} + \underset{(H_2EDTA)}{H_2Y^{2-}} \longrightarrow \underset{\text{Colourless}}{MY^{2-}} + \underset{\text{Blue}}{HIn^{2-}} + H^{\oplus}$$

Ca-EDTA and Mg-EDTA complexes are stable at pH = 8–10, the pH of solution during titration must be maintained at 10 (by $NH_4OH + NH_4Cl$ buffer). Hence, Ca^{2+} ions do not form a sufficiently stable complex with eriochrome black-T. Mg-EDTA complex is added to the titration flask if the sample either does not contain sufficient Mg^{2+} ions (or does not contain at all) to produce a sharp colour change at the end point. Reactions are:

$$Ca^{2+} + H_2Y^{2-} \longrightarrow CaY^{2-} + 2H^{\oplus}$$
$$Mg^{2+} + H_2Y^{2-} \longrightarrow MgY^{2-} + 2H^{\oplus}$$
$$Mg^{2+} + HIn^{2-} \longrightarrow MgIn^{\ominus} + H^{\oplus}$$
$$\underset{\text{Wine red}}{MgIn^{\ominus}} + \underset{\text{Colourless}}{H_2Y^{2-}} \longrightarrow \underset{\text{Colourless}}{MgY^{2-}} + \underset{\text{Blue}}{HIn^{2-}} + H^{\oplus}$$

(at the end point)

From the above reaction, it is clear that
1 mol of $Na_2H_2EDTA \equiv$ 1 mol of Ca^{2+}
= 1 mol of Mg^{2+} ions

$\therefore \quad M_1V_1 = M_2V_2$

(M_1 and M_2 are the molarities of EDTA salt and metal ion solutions, respectively, and V_1 and V_2 are their volumes, respectively.)

ILLUSTRATION 3.11

0.093 g of Na_2H_2 EDTA·$2H_2O$ is dissolved in 250 mL of aqueous solution. A sample of hard water containing Ca^{2+} and Mg^{2+} ions is titrated with the above EDTA solution using a buffer of $NH_4OH + NH_4Cl$ using eriochrome black-T as indicator. 10 mL of the above EDTA solution requires 10 mL of hard water at equivalence point.

Another sample of hard water is titrated with 10 mL of above EDTA solution using KOH solution (pH = 12). Using murexide indicator, it requires 40 mL of hard water at equivalence point.

a. Calculate the amount of Ca^{2+} and Mg^{2+} present in 1 L of hard water.

b. Calculate the hardness due to Ca^{2+}, Mg^{2+} ions and the total hardness of water in ppm of $CaCO_3$.
(Given: MW(EDTA salt) = 372 g mol^{-1}, MW($CaCO_3$) = 100 g mol^{-1})

Sol.

a. **Case I:** Using eriochrome black-T indicator

$$\text{M of EDTA solution} = \frac{0.093 \times 1000}{372 \times 250} = 0.001 \text{ M}$$

Volume of EDTA used = 10 mL

Volume of water sample = 40 mL

$M_1V_1(\text{EDTA}) = M_2V_2$ (Ca^{2+} and Mg^{2+} in hard water)

$0.001 \times 10 = M_2 \times 10$

$M_2 = 0.001$

$\therefore$ Molarities of ($Ca^{2+} + Mg^{2+}$) ions = 0.001 M
= 1.0 mmoles L^{-1}

Case II: Using murexide indicator

$M_1V_1(\text{EDTA}) = M_2V_2(\text{Hard water})$

$0.001 \times 10 = M_2 \times 40$

$M_2 = 0.25 \times 10^{-3} = 0.25$ mmol L^{-1}

$\therefore$ Total mmol L^{-1} of Ca^{2+} and Mg^{2+} = 1.0

mmol L^{-1} of Mg^{2+} = 1.0 – 0.25 = 0.75 mmol L^{-1}

mmol L^{-1} of Ca^{2+} = 0.25 mmol L^{-1}

$\therefore$ Amount of Ca^{2+} $L^{-1} \Rightarrow 0.25 \times 40 \times 10^{-3} = 0.01$ g L^{-1}

Amount of Mg^{2+} $L^{-1} \Rightarrow 0.75 \times 24 \times 10^{-3} = 0.018$ g L^{-1}

b. [MW ($CaCO_3$) = 100 g mol^{-1}]

Total mmol of Ca^{2+} and Mg^{2+} ions L^{-1}
= 1.0 = 0.001 mol L^{-1}
= 0.001 M

0.1 mol of Ca^{2+} and Mg^{2+} ≡ 0.1 mol $CaCO_3$ L^{-1}

$$\equiv \frac{0.001 \times 100 \times 10^6}{10^3}$$

≡ 100 ppm

$\therefore$ Total hardness due to Ca^{2+} and Mg^{2+} ions of the sample in gram of $CaCO_3$ in 10^6 mL of H_2O

$$= \frac{\text{Total M} \times \text{MW } (CaCO_3) \times 10^6}{10^3}$$

Hardness due to Ca^{2+} ions of the sample in gram of $CaCO_3$ in 10^6 mL of H_2O = $\dfrac{0.25 \times 10^{-3} \times 100 \times 10^6}{10^3}$ = 25 ppm

Hardness due to Mg^{2+} ions of the sample in gram of $CaCO_3$ in 10^6 mL of H_2O = 100 – 25 = 75 ppm

ILLUSTRATION 3.12

A 50 mL sample of hard water containing Ca^{2+} and Mg^{2+} ions is titrated with 50 mL 0.005 M EDTA solution at pH = 10, using eriochrome black-T indicator to reach equivalence point. In an equal another amount of hard water sample, Mg^{2+} ions are precipitated as $Mg(OH)_2$ by adding suitable amount of NaOH. The solution, after precipitation of $Mg(OH)_2$, is stirred and then titrated with EDTA solution using calcon as indicator, and it requires 10 mL of above EDTA solution to reach equivalence point.

a. Calculate the strength of Ca^{2+} and Mg^{2+} ions present in hard water.

b. Calculate the hardness due to Ca^{2+} ions in ppm of $CaCO_3$.

c. Calculate the hardness due to Mg^{2+} ions in ppm of $CaCO_3$.

d. Calculate the total hardness of water in ppm of $CaCO_3$.

Sol.

a. **Case I: Using eriochrome black-T indicator**

$M_1V_1(\text{EDTA}) = M_2V_2$ (Ca^{2+} and Mg^{2+} in H_2O)

$50 \times 0.005 = M_2 \times 50$

M_2 of Ca^{2+} and Mg^{2+} = 0.005 M = 5 m mol L^{-1}

Case II: Using calcon indicator

$M_1V_1(\text{EDTA}) = M_2V_2(Ca^{2+} \text{ in } H_2O)$

$10 \times 0.005 = M_2 \times 50$

M_2 of $Ca^{2+} = 10^{-3}$M = 1.0 m mol L^{-1}

mmol L^{-1} of Mg^{2+} = 5 – 1 = 4 m mol L^{-1}

Strength of $Mg^{2+} = 4 \times 24 \times 10^{-3} = 0.096$ g L^{-1}

Strength of $Ca^{2+} = 1 \times 40 \times 10^{-3} = 0.04$ g L^{-1}

b. Hardness due to Ca^{2+} ions of the sample in gram of $CaCO_3$ in 10^6 mL of H_2O

$$= \frac{\text{M } (Ca^{2+}) \times \text{MW } (CaCO_3) \times 10^6}{10^3}$$

$$= \frac{10^{-3} \times 100 \times 10^6}{10^3} = 100 \text{ ppm}$$

c. Hardness due to Mg^{2+} ions of the sample in g of $CaCO_3$ in

$$10^6 \text{ mL of } H_2O = \frac{\text{M } Mg^{2+} \times \text{MW } (CaCO_3) \times 10^6}{10^3}$$

$$= \frac{4 \times 10^{-3} \times 100 \times 10^6}{10^3} = 400 \text{ ppm}$$

d. Total hardness

$$= \frac{\text{M}(Ca^{2+} \text{ and } Mg^{2+}) \times \text{MW}(CaCO_3) \times 10^6}{10^3}$$

$$= \frac{5 \times 10^{-3} \times 100 \times 10^6}{10^3} = 500 \text{ ppm}$$

(Alternatively, Total hardness = Hardness due to Ca^{2+} + Hardness due to Mg^{2+} = 100 + 400 = 500 ppm)

3.7.2.9 Determination of temporary and permanent hardness of water separately

If a water sample is boiled for some time, the bicarbonates of Ca and Mg (which causes *temporary hardness*) are precipitated as white insoluble carbonates and are removed by filtration and weighed. The filtered water sample may now be titrated with

EDTA salt, which gives only *permanent hardness*. The temporary hardness can be manipulated by subtracting the permanent hardness from the total hardness of water sample.

Procedure: First, the total hardness of water sample is determined. Take the water sample and boil it for 30 min. Filter it through a Whatman number 1 filter paper. The insoluble $MgCO_3$ and $CaCO_3$ (formed from their bicarbonates) get removed.

Take the filtered sample of water and then add 2 mL of buffer solution ($NH_4OH + NH_4Cl$), 5 mL of Mg-EDTA complex solution (mandatory), and five drops of the indicator eriochrome black-T. The colour must be *wine red* at this stage. Titrate with EDTA salt solution from a burette to a pure *blue colour*.

This reading of burette gives the volume of EDTA solution used in the determination of permanent hardness.

Temporary hardness = Total hardness – Permanent hardness

$$= \frac{M(Ca^{2+} \text{ and } Mg^{2+}) \times MW\ CaCO_3 \times 10^6}{10^3}$$

$= ...$ ppm of $CaCO_3$

Permanent hardness of the given water sample

$$= \frac{M(Ca^{2+} \text{ and } Mg^{2+}) \text{ after heating} \times MW\ (CaCO_3) \times 10^6}{10^3}$$

$= ...$ ppm of $CaCO_3$

ILLUSTRATION 3.13

A 1mL sample of hard water is titrated with 500 mL of 0.001 M EDTA solution at pH = 10, using eriochrome black-T indicator to reach equivalence point.

An equal another amount of hard water sample is boiled for 30 min. After filtration and cooling, the same sample is titrated with 200 mL of 0.001 M EDTA solution at pH = 10 using Mg-EDTA complex solution and erichrome black-T indicator to reach equivalence point.

a. Calculate the total hardness of water sample (temporary + permanent) in ppm of $CaCO_3$.
b. Calculate the permanent hardness of water sample in ppm of $CaCO_3$.
c. Calculate the temporary hardness of water sample in ppm of $CaCO_3$.

Sol.

a. Total hardness (first titration):

$M_1V_1(\text{EDTA}) = M_2V_2$ (Total Ca^{2+} and Mg^{2+} in temporary and permanent hardness)

$500 \times 0.001 = M_2 \times 100$

$M_2 = 0.005$ (Total Ca^{2+} and Mg^{2+})

$$\text{Total hardness in ppm of } CaCO_3 = \frac{0.005 \times 100 \times 10^6}{10^3}$$

$$= 500 \text{ ppm}$$

b. Permanent hardness (second titration):

$M_1V_1(\text{EDTA}) = M_2V_2$ (Total Ca^{2+} and Mg^{2+} due to permanent hardness)

$200 \times 0.001 = M_2 \times 100$

$M_2 = 0.002$

(Total Ca^{2+} and Mg^{2+} in permanent hardness)

Permanent hardness in ppm of $CaCO_3$

$$= \frac{0.002 \times 100 \times 10^6}{10^3} = 200 \text{ ppm}$$

c. Temporary hardness in ppm of $CaCO_3 = 500 - 200$
$= 300$ ppm

CONCEPT APPLICATION EXERCISE 3.1

1. If water contains 10 ppm of $MgCl_2$ and 8 ppm of $CaSO_4$, calculate the ppm of $CaCO_3$.
2. A 100 mL of tap water was titrated with M/50 HCl with methyl orange as indicator. If 30 mL of HCl were required, calculate the hardness of $CaCO_3$ per 10^5 parts of water. The hardness is temporary.
3. In the determination of hardness of a sample of water, the following results were obtained:
   Volume of sample of H_2O = 100 mL
   Volume of N/50 Na_2CO_3 added to it = 20 mL
   Volume of N/50 H_2SO_4 used to back titrate the unreacted Na_2CO_3 = 10 mL
   Calculate the hardness of water in g L^{-1}.
4. An exhausted zeolite bed was revived by 250 L of NaCl solution containing 50 g L^{-1} of NaCl solution. How many litres of hard water of hardness 250 ppm can be softened on the zeolite bed?

ANSWERS

1. 16.45 **2.** 30 g **3.** 0.1 g L^{-1} **4.** 42735 L

3.8 HEAVY WATER (D_2O)

Heavy water or deuterium oxide (D_2O) was discovered in 1932, by Urey, an American chemist. He showed that ordinary water contains one part of heavy water in 6000 parts of it.

Heavy water is found in minute quantities in rain water, on the leaves of banana trees and in the last remain obtained by the melting of snow by sun on the hills, as in Himalayans.

3.8.1 PREPARATION OF HEAVY WATER

Heavy water is mainly prepared from ordinary water as follows:

1. **By multistage electrolysis of ordinary water:** Taylor, Eyring and Frost process (1993).

   Principle: This method is based on the principle that when ordinary water containing calculated amount of NaOH is electrolysed, protium (or H_2) is liberated more readily as compared to deuterium (D_2) due to the following:

   a. $H^{\oplus}$ is smaller in size as compared to $D^{\oplus}$, hence $H^{\oplus}$ has more mobility or speed as compared to $D^{\oplus}$.
   b. Discharge potential of $H^{\oplus}$ is less than discharge potential of $D^{\oplus}$, hence $H^{\oplus}$ ions are discharged at cathode more readily than $D^{\oplus}$ ions.

c. Hydrogen atoms combine more readily to form molecular hydrogen as compared to deuterium atoms, which combine less readily to form molecular deuterium.

Due to the above reasons, as the electrolysis continues, the concentration of heavy water in ordinary water gradually increases. If electrolysis is continued till only a small volume of the water remains, then almost pure D_2O is obtained.

Approximately, 29000 litres of water is electrolysed to get 1 L of 99% pure D_2O.

The electrolytic cell used for the preparation of heavy water is shown in Fig. 3.8, and it was designed by Brown, Degget and Urey. It consists of a steel cell whose dimensions are 45 cm long and 10 cm in diameter. The steel cell itself acts as cathode, while a perforated cylindrical sheet of nickel acts as an anode.

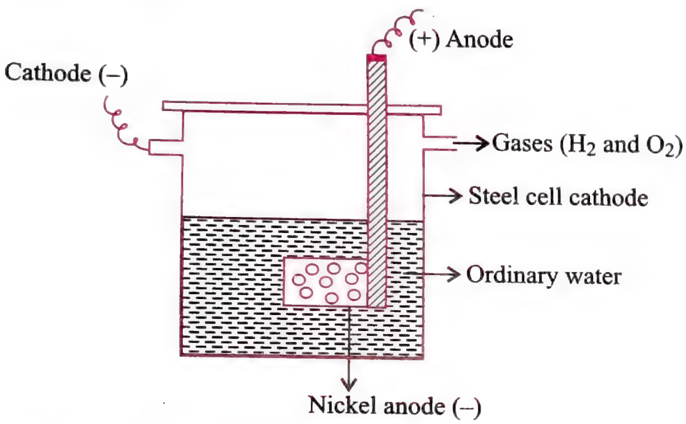


Fig. 3.8 Electrolytic cell for the preparation of heavy water

The electrolysis is completed in seven stages and in actual practice a large number of such cells are employed. In India, heavy water is manufactured by electrolysis of ordinary water at:

i. Nangal in Punjab

ii. Bhabha Atomic Research Centre (BARC), Trombay, in Bombay (Maharashtra)

2. **By fractional distillation of ordinary water:** The boiling points of ordinary and heavy water are 373.42 K (or 101.42°C) respectively at normal atmospheric pressure. *This difference in the boiling point forms the basis of preparation of heavy water by fractional distillation of ordinary water.* Since the difference in boiling point is very small, a very long, i.e. 13 m, fractionating column is employed for fractional distillation.

3. **By fractional freezing of ordinary water:** The freezing points of ordinary and heavy water are 0°C and 3.82°C respectively. Due to the difference in their freezing points, they are separated by the fractional freezing. The process is repeated a number of times.

3.8.2 Properties of Heavy Water

3.8.2.1 Physical Properties

The physical properties of heavy water are as follows:

1. Heavy water is colourless, odourless and tasteless mobile liquid like ordinary water but it is heavier than ordinary water.

2. There is marked difference in the molecular mass of ordinary water and heavy water. Heavy water has greater molecular mass as compared to heavy water and thus a marked compared to heavy water and thus a marked difference in physical properties of the two liquids has been observed.

   Furthermore, the dielectric constant of heavy water is lower than that of ordinary water, hence ionic constants are less soluble in heavy water.

3.8.2.2 Chemical Properties

Heavy water behaves like ordinary water in most of the chemical properties. However, heavy water, D_2O, reacts more slowly than ordinary water, H_2O. Some important chemical properties of D_2O are as follows:

1. **Electrolysis:** The solution of D_2O containing P_2O_5 or Na_2CO_3 on electrolysis gives D_2 at cathode and O_2 at anode. Addition of small amount of P_2O_5 or Na_2CO_3 to D_2O makes its electrical conductor.

$$2D_2O \xrightarrow{\text{Electrolysis}} \underset{\text{(At cathode)}}{2D_2} + \underset{\text{(At anode)}}{O_2}$$

2. **Reaction with alkali and alkaline earth metals:** D_2O, on reaction with alkali and alkaline earth metals produce D_2 and heavy alkalis.

$$2Na + 2D_2O \longrightarrow \underset{\text{Sodium deuteroxide}}{2NaOD} + D_2$$

$$Ca + 2D_2O \longrightarrow \underset{\text{Calcium deuteroxide (heavy alkalis)}}{Ca(OD)_2} + D_2$$

3. **Reaction with metallic oxides:** D_2O reacts slowly with metallic oxides (i.e. basic oxides) such as Na_2O, CaO etc. to form heavy alkalis.

$$Na_2O + D_2O \longrightarrow \underset{\text{Sodium deuteroxide}}{2NaOD}$$

$$CaO + D_2O \longrightarrow \underset{\text{Calcium deuteroxide}}{Ca(OD)_2}$$

4. **Reaction with non-metallic oxides:** D_2O reacts slowly with non-material oxides (i.e. acidic oxides) such as N_2O_5, SO_3 etc. to form deutero-acids.

$$\underset{\text{Dinitrogen pentoxide}}{N_2O_5} + D_2O \longrightarrow \underset{\text{Deuteronitric acid}}{2DNO_3}$$

$$\underset{\text{Sulphur trioxide}}{SO_3} + D_2O \longrightarrow \underset{\text{Deuterosulphuric acid}}{D_2SO_4}$$

$$\underset{\text{Phosphorous pentoxide}}{P_4O_{10}} + 6D_2O \longrightarrow \underset{\text{Deuterophosphoric acid}}{4D_3PO_4}$$

5. **Reaction with metallic nitrides, phosphides, arsenides and carbides:** D_2O reacts with metallic nitrides, phosphide,

arsenides and carbides to give corresponding deutero compounds.

$$\underset{\text{Magnesium nitride}}{Mg_3N_2} + 6D_2O \longrightarrow \underset{\text{Magnesium deuteroxide}}{3Mg(OD)_2} + \underset{\text{Deuteroammonia}}{ND_3}$$

$$\underset{\text{Aluminium nitride}}{2AlN} + 6D_2O \longrightarrow \underset{\text{Aluminum deuteroxide}}{2Al(OD)_3} + \underset{\text{Deutero ammonia}}{2\,ND_3}$$

$$\underset{\text{Calcium phosphide}}{Ca_3P_2} + 6D_2O \longrightarrow \underset{\text{Calcium deuteroxide}}{3Ca(OD)_2} + \underset{\text{Deuterophosphine}}{2PD_3}$$

$$\underset{\text{Sodium arsenide}}{Na_3As} + 3D_2O \longrightarrow \underset{\text{Sodium deuteroxide}}{3\,NaOD} + \underset{\text{Deuteroarsine}}{AsD_3}$$

$$\underset{\text{Calcium carbide}}{CaC_2} + 2D_2O \longrightarrow \underset{\text{Calcium deuteroxide}}{Ca(OD)_2} + \underset{\text{Deuteroacetylene}}{C_2D_2}$$

$$\underset{\text{Aluminium carbide}}{Al_4C_3} + 12\,D_2O \longrightarrow 4Al(OD)_3 + \underset{\text{Deuteromethane}}{2CD_4}$$

6. **Exchange reactions:** D_2O reacts with a number of compounds containing labile hydrogen atoms, in such reactions, H atoms are completely or partially replaced by D. Hence these reactions are known as exchange reactions.

   If the compound contains ionic (i.e. polar) hydrogen atoms, the exchange reaction occurs more readily. For example

   $$NaOH + D_2O \rightleftharpoons NaOD + HOD$$
   $$HCl + D_2O \rightleftharpoons DCl + HOD$$
   $$NH_4Cl + D_2O \rightleftharpoons ND_4Cl + 4HOD$$

   The exchange reactions between NH_4Cl and D_2O takes place in the following steps:

   $$NH_4Cl + D_2O \rightleftharpoons NH_3DCl + HOD$$
   $$NH_4DCl + D_2O \rightleftharpoons NH_2D_2Cl + HOD$$
   $$NH_2D_2Cl + D_2O \rightleftharpoons NHD_3Cl + HOD$$
   $$NHD_3Cl + D_2O \rightleftharpoons ND_4Cl + HOD$$
   $$\overline{NH_4Cl + 4D_2O \rightleftharpoons ND_4Cl + 4HOD}$$

   If the compound contains non-ionic hydrogen atom, the exchange reaction takes place slowly and requires the presence of a catalyst, For example

   $$C_6H_6 + 3D_2O \xrightarrow[200°C]{\text{Ni on Kieselguhr}} \underset{\text{Hexadeutero benzene}}{C_6D_6} + 3H_2O$$

7. **Deuterolysis:** As water brings hydrolysis of certain inorganic chlorides and some other salts, in a similar way, deuterium also gives same reactions, known as deuterolysis.

   $$AlCl_3 + 3D_2O \longrightarrow Al(OD)_3 + 3DCl$$
   $$SiCl_4 + 4D_2O \longrightarrow D_4SiO_4 + 4DCl$$
   $$BiCl_3 + D_2O \longrightarrow BiOCl + 2DCl$$
   $$BaS + 2D_2O \longrightarrow Ba(OD)_2 + D_2S$$

8. **Formation of Deuterates:** Ordinary water gets associated with salts to form the crystalline salts called hydrates. Similarly heavy water also gets associated with salts to form crystalline salts known as deuterates or deutero-hydrates. For example, $BeCl_2 \cdot 4D_2O$, $CuSO_4 \cdot 5D_2O$, $COCl_2 \cdot 6D_2O$, $MgSO_4 \cdot 7D_2O$ etc.

9. **Physiological effects:** It has been established that heavy water of high concentration retards the growth of plants and animals. Few examples are:

   a. Lewis has shown that tobacco seeds do not grow in heavy water, but under similar conditions, they develop well in ordinary water.

   b. Mice and rats on drinking D_2O feel more and more thirsty.

   c. Pure D_2O kills small fish, tadpoles and mice, when fed on them.

Taylor has shown that heavy water has germicide and bactericide properties. Water containing small amount of D_2O acts as a tonic and stimulates vegetable growth. Although D_2O is injurious to health, certain moulds have been found to develop better in heavy water than in ordinary water.

Heavy water is injurious to human beings, animals and plants, since it slows down the reactions occurring in them. Hence heavy water does not support life as ordinary water.

3.8.3 USES

1. **As a tracer compound:** D_2O is widely used as a tracer compound to study the reaction mechanism in organic chemistry. D_2O has also been used to study the structure of some oxyacids of phosphorous such as H_3PO_2 and H_3PO_3 by finding the number of ionic hydrogen atoms in these compounds.

2. **As a moderator:** Substances which are used to slow down the speed of neutrons are called moderators. The speed of neutrons is slowed down by passing them through D_2O, and hence D_2O acts as a moderator.

3. **For the preparation of deuterium:** D_2 can be prepared as follows:

   a. Electrolysis of D_2O

   $$2D_2O \longrightarrow 2D_2 + O_2$$

   b. By the action of sodium metal on D_2O

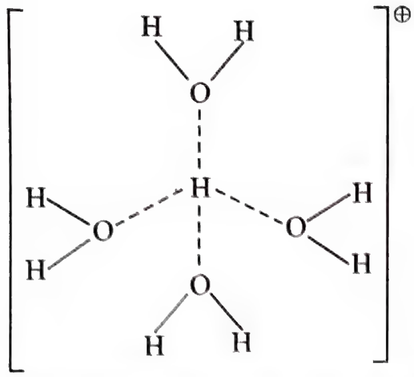
   $$2D_2O + 2Na \longrightarrow 2NaOH + D_2$$

ILLUSTRATION 3.14

a. What does $[H_9O_4]^{\oplus}$ stand for? Draw its structure.
b. Can sodium bicarbonate make water hard?
c. Hard water is softened before using in boilers. Why?
d. What is sequestration? How is hard water made soft by sequestration?

Sol.

a. $[H_9O_4]^{\oplus}$ stands for hydrated proton. In $[H_9O_4]^{\oplus}$, $H^{\oplus}$ is tetrahedrally surrounded by four water molecules.



b. Hardness of water can be created due to sodium bicarbonate because soaps themselves are sodium salts of fatty acids which are soluble in water.

c. Hard water on boiling gives white precipitate of $MgCO_3$, $CaCO_3$ and $CaSO_4$ which form scales in boilers. The formation of these boiler scales causes rapid deterioration of the boiler due to over heating. Further, boiler scales are non-conducting. Hence, more fuel is consumed. Therefore, to prevent formation of boiler scales, hard water is softened before using in boilers.

d. 'Sequestration' means to render ineffective. The hardness of water is due to the presence of Ca^{2+} and Mg^{2+} ions. These ions are rendered ineffective by treating with calgon, i.e., sodium hexametaphosphate. On addition of calgon to hard water, the Ca^{2+} and Mg^{2+} ions present in it, combines with calgon to form soluble compounds of calcium and magnesium salts.

$$2CaCl_2 + \underset{\text{Sodium hexametaphosphate}}{Na_2[Na_4(PO_3)_6]} \longrightarrow \underset{\text{Complex}}{Na_2[Ca_2(PO_3)_6]} + 4\,NaCl$$

$$2MgSO_4 + Na_2\,[Na_4(PO_3)_6] \longrightarrow \underset{\text{Complex}}{Na_2[Mg_2(PO_3)_6]} + 2Na_2SO_4$$

These complex calcium and magnesium ions do not form any precipitate with soap and hence readily produces lather with soap solution. In this way, hard water is softened by sequestration.

ILLUSTRATION 3.15

a. Water extinguishes most fires, but it does not extinguish petrol fires. Explain.

b. Soft water lathers with soap, but not hard water. Why?

Sol.

a. Water extinguishes most fires by lowering down the temperature of the burning material. But in case of petrol fire, since petrol is lighter than water, it floats over water and hence fire spreads instead of extinguishing.

b. Hard water contains calcium and magnesium salts. These react with soap to form insoluble calcium and magnesium salts of fatty acids, i.e. form scum and not lather.

$$2RCOONa + Ca^{2+} \longrightarrow (RCOO)_2\,Ca \downarrow + 2Na^{\oplus}$$

$$2RCOONa + Mg^{2+} \longrightarrow (RCOO)_2\,Mg \downarrow + 2Na^{\oplus}$$

ILLUSTRATION 3.16

a. A small amount of acid or alkali is added before electrolysis of water. Why?

b. What happens when:

i. Hydrolith is treated with water.

ii. Heavy water reacts with aluminium carbide.

Sol.

a. Pure water being a weak electrolyte and feebly ionised is a bad conductor of electricity. In order to make it good conductor, a small amount of acid or alkali is added before electrolysis.

b. i. Hydrolith, i.e. CaH_2 on hydrolysis gives calcium hydroxide, $Ca(OH)_2$ with the evolution of dihydrogen gas, H_2.

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2\uparrow$$

ii. Deuteromethane is evolved when heavy water reacts with aluminium carbide.

$$\underset{\text{Aluminium carbide}}{Al_4C_3} + \underset{\text{Heavy water}}{D_2O} \longrightarrow 4Al(OH)_3\downarrow + \underset{\text{Deuteromethane}}{3CD_4}$$

ILLUSTRATION 3.17

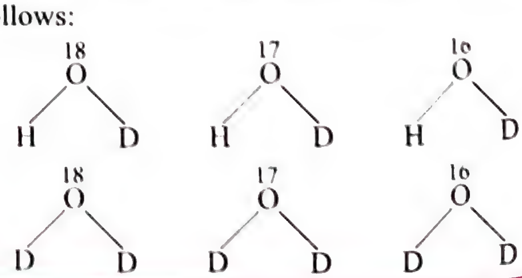
a. Naturally hard water is usually preferred in drinking and soft water in working. Why?

b. How many types of heavy water are possible? Write down formulae of all possible heavy water molecules.

Sol.

a. Soft water is usually acidic and contains $Na^{\oplus}$ ions in place of di- and trivalent metal ions. An increased intake of $Na^{\oplus}$ is known to be related to heart disease and moreover the acidic soft water is more likely to attack metallic pipes, resulting in the solution of dangerous ions such as Pb^{2+}. One way to avoid $Na^{\oplus}$ ions in drinking water and to use less soap when washing would be to drink naturally hard water and work in soft water.

b. These are six possible heavy water molecules, which are as follows:



3.9 HYDROGEN PEROXIDE (H_2O_2)

Hydrogen peroxide (H_2O_2) occurs in minute amount in air, water, snow and juices of certain plants. Hydrogen peroxide was first prepared in 1818, by the French chemist, Louis Jacques Thenard by the action of dilute acids on barium peroxide.

PREPARATION

Laboratory methods of preparation of H_2O_2

From sodium peroxide (Merck's method): By gradually adding calculated amount of sodium peroxide (Na_2O_2) to an ice-cold solution of H_2SO_4 (20%).

$Na_2O_2 + H_2SO_4 \longrightarrow NaSO_4 + H_2O_2$

On cooling, Na_2SO_4 separates out as $Na_2SO_4 \cdot 10H_2O$ crystals and the resulting solution contains ~ 30% H_2O_2. A pure sample of H_2O_2 can be obtained by vacuum distillation.

From barium peroxide:

i. By passing CO_2 through a thin paste of BaO_2 in ice-cold water.

$BaO_2 + CO_2 + H_2O \longrightarrow BaCO_3\downarrow + H_2O_2$

On filtration, white precipitate of barium carbonate, $BaCO_3$ separates out leaving behind a solution of H_2O_2.

ii. By the action of cold dilute sulphuric acid on hydrated barium peroxide.

$$BaO_2 \cdot 8H_2O + H_2SO_4 \rightarrow \underset{\text{Barium sulphate}}{BaSO_4\downarrow} + H_2O_2 + 8H_2O$$

The white precipitate of $BaSO_4$ is removed by filtration thus leaving behind a solution of H_2O_2 (5%).

In this method, *$BaO_2 \cdot 8H_2O$ is used instead of BaO_2*, the white ppt. of $BaSO_4$ formed deposits on BaO_2, thus forming a protective layer and hence prevent any further reaction between BaO_2 and H_2SO_4.

Limitation of this method: H_2O_2 prepared by this method cannot be stored for long time, as it contains appreciable amount of Ba^{2+} ions in the form of dissolved barium persulphate, which catalyses the decomposition of H_2O_2. Decomposition of H_2O_2 is also catalysed by H_2SO_4, hence weaker acid like CO_2 should be used.

iii. By the action of phosphoric acid (H_3PO_4) on hydrated barium peroxide.

$$3(BaO_2 \cdot 8H_2O) + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2\downarrow + 3H_2O_2 + 24H_2O$$

Barium phosphate, $Ba_3(PO_4)_2$ precipitate is decomposed by dil H_2SO_4 to give H_3PO_4, which can be reused.

$Ba_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3BaSO_4\downarrow + 2H_3PO_4$

iv. H_3PO_4 is preferred over H_2SO_4 in preparation of H_2O_2 from peroxides.

H_2SO_4 acts as a catalyst for the decomposition of H_2O_2. Therefore, some weaker acids such as H_3PO_4, for preparation of H_2O_2 from peroxide.

$$3BaO_2 + 2H_3PO_4 \longrightarrow \underset{\text{(Insoluble)}}{Ba_3(PO_4)_2} + 3H_2O_2$$

c. By the hydrolysis of Caro's acid:

$$\underset{\text{Peroxomono sulphuric acid or Caro's acid}}{H_2SO_5} + H_2O \longrightarrow H_2SO_4 + H_2O_2$$

2. Industrial methods of preparation of H_2O_2

a. By the electrolysis of 50% solution of H_2SO_4: On electrolysis cold 50% solution of H_2SO_4 at high current density in an electrolytic cell using platinum wire as anode and graphite as cathode, the following reactions take place:

$H_2SO_4 \rightleftharpoons 2H^{\oplus} + H_2SO_4^{\ominus}$ (Ionisation)

At cathode: $2H^{\oplus} + 2e^{\ominus} \longrightarrow H_{2(g)}$ (Reduction) ...(3.1)

At anode: $2HSO_4^{\ominus} \longrightarrow H_2S_2O_8 + 2e^{\ominus}$ (Oxidation) ...(3.2)

$H_2O \longrightarrow 2H+ \frac{1}{2}O_2 + 2e^{\ominus}$ (Oxidation) ...(3.3)

Note: With high conc 1' H_2SO_4, Eq. (3.2) is preferred and with very dilute H_2SO_4 Eq. (3.3) is preferred but with 50% aqueous H_2SO_4 both Eq. (3.2) and (3.3) occur at anode, so O_2 is produced as by product.

Peroxodisulphuric acid or Marshall's acid ($H_2S_2O_8$) formed at anode is withdrawn and distilled with dil. H_2SO_4 under reduced pressure.

$$\underset{\text{Peroxodisulphuric acid}}{H_2S_2O_8} + H_2O \xrightarrow[\text{(partial hydrolysis)}]{\text{dil } H_2SO_4} \underset{\text{Peroxomono-sulphuric acid}}{H_2SO_5} + H_2SO_4$$

$$H_2SO_5 + H_2O \xrightarrow{\text{Complete hydrolysis}} H_2SO_4 + H_2O_2$$

b. By electrolysis of equimolar mixture of ammonium sulphate in H_2SO_4: By this method, a more concentrated solution of H_2O_2 is obtained as compared to electrolysis of 50% solution of H_2SO_4.

$$\underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4} + H_2SO_4 \longrightarrow \underset{\text{Ammonium hydrogensulphate}}{2NH_4HSO_4}$$

$2NH_4HSO_4 \longrightarrow 2H^{\oplus} + 2NH_4SO_4^{\ominus}$

At anode: $2NH_4SO_4^{\ominus} \longrightarrow \underset{\text{Ammonium persulphate}}{(NH_4)_2S_2O_8} + 2e^{\ominus}$ (Oxidation)

At cathode: $2H^{\oplus} + 2e^{\ominus} \longrightarrow H_2$ (Reduction)

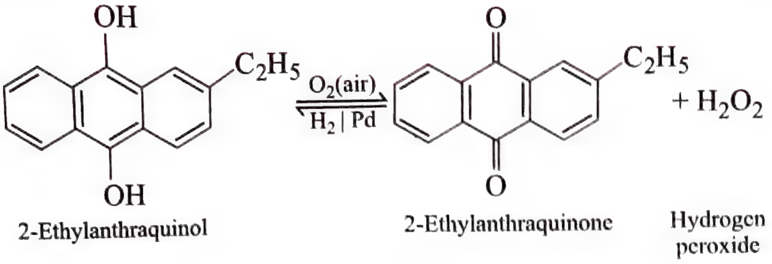
Ammonium persulphate formed at anode is distilled with water to give H_2O_2.

$(NH_4)_2S_2O_8 + 2H_2O \longrightarrow 2NH_4HSO_4 + H_2O_2$

This method is now used for the laboratory preparation of D_2O_2.

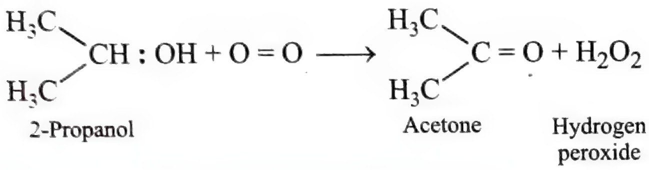
$K_2S_2O_8 + 2D_2O \longrightarrow 2KDSO_4 + D_2O_2$

c. By auto-oxidation of 2-ethylanthraquinol: The process involves a cycle of reactions. The net reaction is the union of H_2 and O_2 to yield H_2O_2.



The H_2O_2 (~1%) thus formed is extracted with water and concentrated to ~ 30% (by weight) by distillation under reduced pressure. It can be further concentrated to ~85% by careful distillation under reduced pressure. The remaining water can be frozen out to give pure H_2O_2.

d. By the oxidation of 2-propanol: On oxidation at high pressure, 2-propanol gives acetone and hydrogen peroxide.



3.9.2 Methods for Concentrating H_2O_2 Solution

Hydrogen peroxide, obtained by any of the above-mentioned methods is in the form of dilute solution. The concentration of H_2O_2 is quite dangerous, due to its explosive decomposition into H_2O and O_2.

It cannot be concentrated by distillation, as it decomposes much below its boiling point.

$$2H_2O_{2(l)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$$

Further, this decomposition is catalysed by impurities particulary heavy metal ions, dust or rough surfaces.

The dilute H_2O_2 solution is concentrated as follows:

1. **By careful evaporation of the solution:** The dilute H_2O_2 solution is carefully evaporated on a water bath, preferably under reduced pressure and using a fractionating column. As water is more volatile than hydrogen peroxide, water is evaporated first till a 20% H_2O_2 solution is obtained. Since this also results in concentration of impurities in the product and many of these impurities catalyse decomposition. Further, concentration of H_2O_2 beyond 30% evaporation is not advisable.
2. **Distillation under reduced pressure:** The above solution is heated in a distillation flask up to 318 K under reduced pressure (15 mm). At first water, being more volatile, comes out, at ~343 K, H_2O_2 begins to distil out. The solution thus obtained is ~90% pure.
3. **By crystallisation:** Last traces of water in hydrogen peroxide are removed by using freezing mixture comprising solid carbon dioxide (or dry ice) and ether. The whole mass first freezes, but on addition of little frozen solid into concentrated hydrogen peroxide solution, needle-shaped crystals of 100% pure hydrogen peroxide separate out.

3.9.3 Structure of H_2O_2

Hydrogen peroxide, H_2O_2, has a non-planar and non-linear structure (as indicated by its high dipole moment value, μ=2.1D). X-ray studies of solid H_2O_2 molecule has also indicated that the H_2O_2 molecule has a non-planar and non-linear structure in which the two H–O bonds are asymmetrically distributed. According to X-ray studies, the H_2O_2 molecule can be best picturised as shown in Fig. 3.9, in which the two O-atoms can be considered to be lying on the spine of a book opened at an angle of 90.2° (dihedral angle). The molecular dimensions in the gas phase and solid phase are shown in Fig. 3.9.

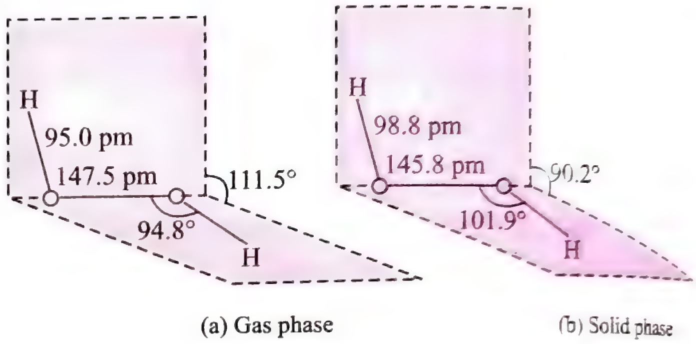
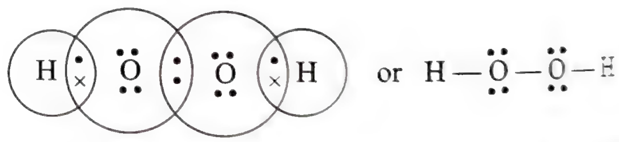


Fig. 3.9 (a) H_2O_2 structure (gas phase) dihedral angle 111.5° and (b) H_2O_2 (solid phase at 110 K)

Lewis structure of H_2O_2 molecule indicates that each of the two O-atoms is linked with H-atoms by σ-bond and has two pairs on it.



The O–O σ bond results from head to head overlap of two sp^3 hybrid orbitals on both the O-atoms and the O–H σ bonds are formed by remaining sp^3 hybrid orbital of O-atom with 1s orbitals of H-atoms as shown in Fig. 3.10.

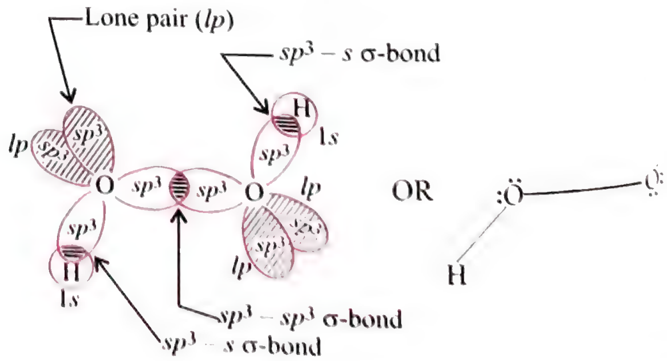


Fig. 3.10 Structure of H_2O_2 showing sp^3 hybridisation of both O-atoms

Repulsion between the two lone pairs on each O-atom forces the O–H and O–O bonds to come closer to each other and thus each of the H–O–O–H bonds angles (= 90.2°) is below the tetrahedral angle (=109.5°). There is also a possibility of some repulsion between the electron pairs on O-atom and those on the other O-atom and this repulsion may account for the fact that O–O bond length

(= 145.8 pm) is greater than the calculated single bond O–O distance, which is equal to double the radius of O-atom.

3.9.4 PHYSICAL PROPERTIES OF H_2O_2

1. Anhydrous H_2O_2 is a colourless syrupy liquid, in thick layers, it gives a blue tinge.
2. Hydrogen peroxide is more dense and more viscous or less volatile as compared to water. H_2O_2 molecules are associated via hydrogen bonding, since the association through hydrogen bonding is more amongst hydrogen peroxide molecules as compared to water molecules. H_2O_2 is more dense and viscous as compared to water.
3. H_2O_2 produces blisters in contact with skin.
4. H_2O_2 boils at 150°C with decomposition,

$$2H_2O_2 \xrightarrow{\Delta} 2H_2O + O_2$$

but it can be distilled under reduced pressure. Since H_2O_2 decomposes on heating, it is not possible to determine its boiling point at atmospheric pressure. But its boiling point has been determined by extrapolation method.

5. H_2O_2 is miscible with water, alcohol and ether in all proportions. With water, it forms a hydrate, $H_2O_2{\cdot}H_2O$ (mp. 221 K). A 3% solution is marketed as 100 volume hydrogen peroxide, indicating that at STP, 10 volumes of oxygen are liberated per mL of the solution. Commercial H_2O_2, marketed as '100 volume' peroxide contains 3% H_2O_2.

3.9.5 CHEMICAL PROPERTIES OF H_2O_2

1. **Decomposition:** Pure H_2O_2 is not very stable and decomposes in the presence of light or on standing or heating.

$$\overset{(1-)}{H_2O_{2(l)}} \longrightarrow \overset{(2-)}{H_2O_{(l)}} + \overset{(0)}{O_{2(g)}}$$

The oxidation state of oxygen in H_2O_2 is –1, it is oxidised to oxidation state of zero in O_2 and is reduced to an oxidation state of –2 in H_2O. Thus, this decomposition is an example of *auto oxidation–reduction* reaction or *disproportionation reaction.*

Decomposition of H_2O_2 occurs slowly, but the presence of finely divided metals, traces of alkali (present in glass containers) accelerates the decomposition, thus they act as *positive catalysts*. Dust (even in very small quantities) induces explosive decomposition. On the other hand, traces of acid, acetanilide, or alcohol deacclerates the decomposition or act as stabilisers. Thus, they act as negative catalysis.

H_2O_2 is therefore not kept in glass bottle, since it gets decomposed by alkali oxides present in glass.

Hence, *H_2O_2 is stored in wax-lined glass or plastic vessels in the presence of stabilisers like urea.*

2. **Oxidising agent:** H_2O_2 acts as a powerful oxidising agent electron acceptor both in the acidic and alkaline medium.

a. In acidic medium:

$$H_2O_2 \xrightarrow{\text{Reduction}} H_2O + [O]$$

Or

$$\underset{(O=-1)}{H_2O_2} + 2H^{\oplus} + 2e^{\ominus} \longrightarrow \underset{(O=-2)}{2H_2O} \qquad E^{\ominus} = +1.77\text{ V}$$

Some typical reactions in acidic medium are as follows:

i. H_2O_2 oxidises lead sulphide, PbS, to lead sulphate, $PbSO_4$.

$$S^{2-} + 4H_2O_2 \longrightarrow SO_4^{2-} + 4H_2O$$

Or

$$\underset{\text{Black}}{PbS_{(s)}} + 4H_2O_{2(l)} \longrightarrow \underset{\text{White}}{PbSO_{4(s)}} + 4H_2O_{(l)}$$

This reaction is employed to restore the colour of old oil paintings, which turn black due to formation of. PbS, by the action of atmospheric H_2S on the white pigment, consisting of basic lead carbonate. $PbCO_3{\cdot}Pb(OH)_2$

ii. H_2O_2 oxidises arsenites, AsO_3^{3-} (As = +3) to arsenates AsO_4^{3-} (As = + 5).

$$\underset{\text{Arsenite ion}}{\overset{(+3)}{AsO_3^{3-}}} + H_2O_2 \longrightarrow \underset{\text{Arsenate ion}}{\overset{(+5)}{AsO_4^{3-}}} + H_2O$$

Or

$$\underset{\text{Sodium arsenite}}{Na_3AsO_3} + H_2O_2 \longrightarrow \underset{\text{Sodium arsenate}}{Na_3AsO_4} + H_2O$$

iii. H_2O_2 oxidises nitrite, $NO_2^{\ominus}$ (N = +3) to nitrite, $NO_3^{\ominus}$ (N = + 5).

$$\underset{\text{Nitrite ion}}{NO_2^{\ominus}} + H_2O_2 \longrightarrow H_2O + \underset{\text{Nitrate ion}}{NO_3^{\ominus}}$$

Or

$$\underset{\text{Potassium nitrite}}{KNO_2} + H_2O_2 \longrightarrow \underset{\text{potassium nitrate}}{KNO_3} + H_2O$$

iv. H_2O_2 oxidises sulphite, SO_3^{2-} (S = + 4) to sulphate, SO_4^{2-} (S = + 6).

$$\underset{\text{Sulphite ion}}{SO_3^{2-}} + H_2O_2 \longrightarrow \underset{\text{Sulphate ion}}{SO_4^{2-}} + H_2O$$

Or

$$\underset{\text{Sodium sulphite}}{Na_2SO_3} + H_2O_2 \longrightarrow H_2O + \underset{\text{Sodium sulphate}}{Na_2SO_4}$$

v. H_2O_2 oxidises sulphide, S^{2-} (S = –2) to sulphur, S (S = 0).

$$H_2O_2 + S^{2-} + 2H^{\oplus} \longrightarrow S + 2H_2O$$

Or

$$H_2O_2 + H_2S \longrightarrow S + 2H_2O$$

vi. H_2O_2 oxidises acidified solution of ferrous, Fe^{2+} (Fe = +2) to ferric, Fe^{3+} (Fe = +3).

$$H_2O_2 + \underset{\text{Ferrous ion}}{2Fe^{2+}} + 2H^{\oplus} \longrightarrow 2H_2O + \underset{\text{Ferric ion}}{2Fe^{3+}}$$

Or

$$H_2O_2 + H_2SO_4 + \underset{\text{Ferrous sulphate}}{2FeSO_4} \longrightarrow \underset{\text{Ferric sulphate}}{Fe_2(SO_4)_3} + 2H_2O$$

Or

$H_2O_2 + H_2SO_4 + 2(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ (Mohr's salt)

$\rightarrow Fe_2(SO_4)_3 + 2(NH_4)_2SO_4 + 8H_2O$

vii. H_2O_2 oxidises acidified solution of iodide, $I^{\ominus}$ ($I^{\ominus} = -1$) to iodine, I_2 ($I = 0$).

$H_2O_2 + 2I^{\ominus} + 2H^{\oplus} \longrightarrow I_2 + 2H_2O$ (Iodide ion; Iodine)

Or

$H_2O_2 + 2KI + H_2SO_4 \longrightarrow K_2SO_4 + I_2 + 2H_2O$ (Potassium Iodide; Iodine)

viii. H_2O_2 oxidises acidified solution of ferrocyanide, $[Fe(CN)]^{4-}$ ($Fe = +2$) to ferricyanide, $[Fe(CN)_6]^{3-}$ ($Fe = +3$).

$2[Fe(CN)_6]^{4-} + H_2O_2 + 2H^{\oplus} \longrightarrow 2[Fe(CN)_6]^{3-} + 2H_2O$

Or

$2K_4[Fe(CN)_6] + H_2SO_4 + H_2O \longrightarrow 2K_3[Fe(CN)_6] + K_2SO_4 + 2H_2O$ (Potassium ferrocyanide; Potassium Ferricyanide)

ix. H_2O_2 oxidises benzene, C_6H_6 to phenol, C_6H_5OH in presence of $FeSO_4$.

(Note: $H_2O_2 + FeSO_4$ is called Fenton's reagent)

$C_6H_6 + H_2O_2 \xrightarrow{FeSO_4} C_6H_5OH + H_2O$

x. H_2O_2 oxidises hydrazine, N_2H_4 ($N = -2$) to nitrogen, N_2 ($N = 0$) in the presence of Cu(II) catalyst.

$3N_2H_4 + 2H_2O_2 \xrightarrow{\text{Cu(II) catalyst}} N_2 + 4H_2O + \text{Heat}$

xi. H_2O_2 oxidises mercury, Hg ($Hg = 0$) to mercurous oxide, HgO ($Hg = +2$) in the presence of H_2SO_4.

$Hg + H_2O_2 \xrightarrow{H_2SO_4} HgO + H_2O$

b. In alkaline medium:

$\underset{(-1)}{H_2O_2} + 2e^{\ominus} \longrightarrow \underset{(-2)}{2\overset{\ominus}{O}H} \qquad E^{\ominus} = +0.87\ V$

Sometimes H_2O_2 is reduced to H_2

$H_2O_2 \longrightarrow H_2 + 2[O]$

Thus H_2O_2 oxidises formaldehyde, HCHO to formic acid, HCOOH in the presence of pyrogallol.

$H_2O_2 \longrightarrow H_2 + 2[O]$

$2[O] + 2HCHO \longrightarrow 2HCOOH$

$2HCHO + H_2O_2 \longrightarrow H_2 + 2HCOOH$

In the dark, this reaction is accompanied by the emission of light, i.e. chemiluminescence.

Some typical reactions in alkaline medium are as follows:

i. H_2O_2 oxidises ferrous, Fe^{2+} ($Fe = +2$) to ferric, Fe^{3+} ($Fe = +3$).

$2Fe^{2+} + H_2O_2 \longrightarrow 2Fe^{3+} + 2\overset{\ominus}{O}H$

ii. H_2O_2 oxidises chromium (III) salts to chromate salts.

$Cr^{3+} + 3H_2O_2 + 10\overset{\ominus}{O}H \longrightarrow 2CrO_4^{2-} + 8H_2O$

Or

$Cr_2(SO_4)_3 + 3H_2O + 10NaOH \longrightarrow 2Na_2CrO_4 + 3Na_2SO_4 + 8H_2O$ (Chromium sulphate; Sodium chromate)

iii. H_2O_2 oxidises Mn(II) salts to manganese dioxide.

$Mn^{2+} + H_2O_2 + 2\overset{\ominus}{O}H \longrightarrow MnO_2 + 2H_2O$

Or

$MnSO_4 + H_2O_2 + 2NaOH \longrightarrow Na_2SO_4 + MnO_2 + 2H_2O$ (Manganese sulphate; Manganese dioxide)

iv. H_2O_2 oxidises ferrous salts to ferric salts.

$2Fe^{2+} + H_2O_2 \longrightarrow 2Fe^{3+} + 2\overset{\ominus}{O}H$

3. **Reducing agent:** H_2O_2 also acts as reducing agent (electron donor) in acidic as well as alkaline medium.

a. In acidic medium:

$H_2O_2 \xrightarrow{\text{Oxidation}} O_2 + 2[H]$

Or

$\underset{(O=-1)}{H_2O_2} \xrightarrow{\text{Oxidation}} \underset{(O=0)}{O_2} + 2H^{\oplus} + 2e^{\ominus}$

Some typical examples in acidic medium are as follows:

i. H_2O_2 reduces hydroxylamine, NH_2OH ($N = -1$) to ammonia, NH_3 ($N = -3$).

$H_2O_2 + NH_2OH \longrightarrow O_2 + NH_3 + H_2O$

ii. H_2O_2 reduces ozone, O_3 to O_2. In this reaction H_2O_2 is oxidised to O_2 and O_3 is reduced to H_2O.

$\underset{(-1)}{H_2O_2} + \underset{(0)}{O_3} \longrightarrow \underset{(-2)}{H_2O} + 2O_2$

iii. H_2O_2 reduces halogens, e.g. Cl_2, Br_2 to respective halogen acid, HCl, HBr.

$H_2O_2 + X_2 \longrightarrow O_2 + 2X^{\ominus} + 2H^{\oplus} \qquad (X = Cl, Br)$

Or

$H_2O_2 + X_2 \longrightarrow 2HX + O_2$

iv. H_2O_2 reduces acidified solution of manganese dioxide, MnO_2 ($Mn = +4$) to Mn(II) salt.

$H_2O_2 + MnO_2 + 2H^{\oplus} \longrightarrow Mn^{2+} + 2H_2O + O_2$

Or

$MnO_2 + H_2SO_4 + H_2O_2 \longrightarrow MnSO_4 + 2H_2O + O_2$

v. H_2O_2 reduces acidified solution of Pb_3O_4 ($Pb = +8/3$) to Pb(II) salt.

$H_2O_2 + Pb_3O_4 + 6H^{\oplus} \longrightarrow 3Pb^{2+} + 4H_2O + O_2$

Or

$H_2O_2 + Pb_3O_4 + 6HNO_3 \longrightarrow 3Pb(NO_3)_2 + 4H_2O + O_2$

vi. H_2O_2 reduces acidified potassium dichromate, $K_2Cr_2O_7$ (Cr = +6) to chromium(III) salt. The orange colour of $K_2Cr_2O_7$ changes to green colour due to formation of Cr(III) salt.

$$Cr_2O_7^{2-} + 8H^{\oplus} + 3H_2O_2 \longrightarrow 2Cr^{3+} + 7H_2O + 3O_2$$

Or

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2O_2 \longrightarrow K_2SO_4 + \underset{\text{(green)}}{Cr(SO_4)_3} + 7H_2O + 3O_2$$

vii. H_2O_2 reduces acidified potassium permanganate, $KMnO_4$ (Mn = +7) to Mn(II) salt. The pink colour of $KMnO_4$ is discharged due to the formation of colourless Mn(II) salt.

$$2\,MnO_4^{\ominus} + 6H^{\oplus} + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

Or

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

viii. H_2O_2 reduces Ag_2O (Ag = +1) to Ag (Ag = 0).

$$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$

ix. H_2O_2 reduces PbO_2 (Pb = +4) to Pb (Pb = 0).

$$PbO_2 + 2H_2O_2 \longrightarrow Pb + 2H_2O + 2O_2$$

x. H_2O_2 reduces hypochlorite, $ClO^{\ominus}$ (Cl = +1) and hypobromite, $BrO^{\ominus}$ (Br = +1) to their corresponding halide, $Cl^{\ominus}$ and $Br^{\ominus}$ (X = –1).

$$H_2O_2 + ClO^{\ominus} \longrightarrow O_2 + Cl^{\ominus} + H_2O$$

Or

$$H_2O_2 + NaOCl \longrightarrow HCl + H_2O + O_2$$

Since, $H_2O + BrO^{\ominus} \longrightarrow O_2 + Br^{\ominus} + H_2O$

Or

$$H_2O_2 + NaOBr \longrightarrow HBr + H_2O + O_2$$

b. In alkaline medium:

$$H_2O_2 + 2\overset{\ominus}{O}H \longrightarrow 2H_2O + O_2 + 2e^{\ominus}$$

Or $\quad H_2O_2 + [O] \longrightarrow H_2O + O_2$

Some typical reactions in alkaline medium are as follows:

i. H_2O_2 reduces potassium permanganate, $KMnO_4$ (Mn = +7) to manganese dioxide, MnO_2 (Mn = +4).

$$2MnO_4^{\ominus} + 3H_2O_2 \longrightarrow 2MnO_2 + 2\overset{\ominus}{O}H + 3O_2 + 2H_2O$$

Or

$$2KMnO_4 + 3H_2O_2 \longrightarrow 2MnO_2 + 2KOH + 3O_2 + 2H_2O$$

ii. H_2O_2 reduces potassium ferricyanide to potassium ferrocyanide.

$$H_2O_2 + 2\overset{\ominus}{O}H + 2[Fe(CN)_6]^{3-} \longrightarrow 2H_2O + O_2 + 2[Fe(CN)_6]^{4-}$$

Or

$$H_2O_2 + 2KOH + 2K_3\,[Fe(CN)_6] \longrightarrow 2H_2O + O_2 + 2K_4[Fe(CN)_6]$$

iii. H_2O_2 reduces silver oxide to silver.

$$\underset{\text{Silver oxide}}{\overset{(1+)}{Ag_2O}} + H_2O_2 \longrightarrow \underset{\text{Silver}}{\overset{(0)}{2Ag}} + H_2O + O_2$$

iv. H_2O_2 reduces lead dioxide to lead monoxide.

$$\underset{\text{Lead dioxide}}{\overset{(2+)}{PbO_2}} + H_2O \longrightarrow \underset{\text{Lead monoxide}}{\overset{(1+)}{PbO}} + H_2O + O_2$$

v. H_2O_2 reduces hypochlorites and hypobromites to chlorides and bromides respectivity.

$$CaOCl_2 + H_2O \longrightarrow CaCl_2 + H_2O + O_2$$

$$NaOBr + H_2O_2 \longrightarrow NaBr + H_2O + O_2$$

vi. H_2O_2 reduces iodine to iodide ion.

$$I_2 + H_2O_2 + 2\overset{\ominus}{O}H \longrightarrow 2I^{\ominus} + 2H_2O + O_2$$

4. Acidic nature: The aqueous solution of H_2O_2 acts as a weak acid. It ionises in water in the following two steps:

$H_2O_2 + H_2O \rightleftharpoons H_3O^{\oplus} + HO_2^{\ominus}$ *(hydroperoxide ion)*...(3.4)

$HO_2^{\ominus} + H_2O \rightleftharpoons H_3O^{\oplus} + O_2^{2-}$ *(peroxide ion)* ...(3.5)

Equations (3.4) and (3.5) can also be written as Eqs. (3.6) and (3.7), respectively.

$H_2O_2 \rightleftharpoons H^{\oplus} + HO_2^{\ominus}$ ...(3.6)

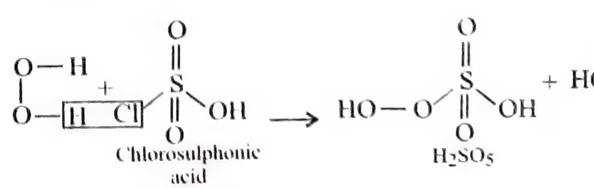
$HO_2^{\ominus} \rightleftharpoons H^{\oplus} + O_2^{2-}$ ...(3.7)

The above equations indicate that H_2O_2 acts as a dibasic acid and hence gives two types of salts *viz. hydroperoxide* (e.g. $NaHO_2$) and peroxide (e.g. Na_2O_2). The acidic character of the aqueous solution of H_2O_2 is confirmed by the fact that it reacts with bases such as NaOH, $Ba(OH)_2$, Na_2CO_3 etc., to form the salt (peroxide).

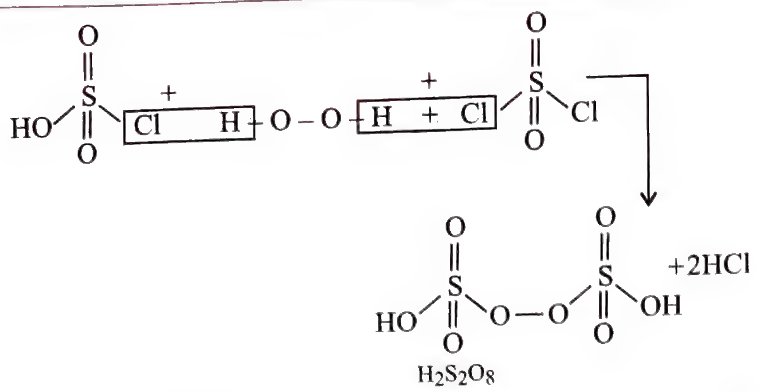
Acid		*Base*		*Salt (peroxide)*
H_2O_2	+	2NaOH	$\longrightarrow$	$Na_2O_2 + 2H_2O$
H_2O_2	+	$Ba(OH)_2$	$\longrightarrow$	$BaO_2 + 2H_2O$
H_2O_2	+	Na_2CO_3	$\longrightarrow$	$Na_2O_2 + H_2O + CO_2$

5. Reaction with chlorosulphonic acid , $ClSO_2OH$:

a. One mole of anhydrous H_2O_2 reacts with one mole of chlorosulphonic acid to give peroxodisulphuric acid or *Caro's acid*, H_2SO_5.



b. One mole of anhydrous H_2O_2 reacts with two moles of chlorosulphonic acid to give peroxodisulphuric acid or *Marshall's acid*, $H_2S_2O_8$.



6. **Reaction with Caro's acid (H_2SO_5):** H_2SO_5 when warmed with H_2O_2, loses O_2 and is converted to H_2SO_4.

$$H_2SO_5 + H_2O_2 \xrightarrow{\Delta} H_2SO_4 + H_2O + O_2\uparrow$$

7. **Reaction with sulphur trioxide (SO_3):** SO_3 on reaction with anhydrous H_2O_2 gives Caro's acid.

$$H_2O_2 + SO_3 \longrightarrow H_2SO_5$$

8. **Reaction with titanium dioxide (TiO_2) in conc H_2SO_4 or titanium sulphate, $Ti(SO_4)_2$:** On addition of H_2O_2 to the solution of TiO_2 in conc H_2SO_4 or to the solution of $Ti(SO_4)_2$, a blue-coloured solution is obtained due to the formation of pertitanic acid, H_2TiO_4. H_2TiO_4 being unstable, decomposes to give bright yellow titanium trioxide, TiO_3.

$$Ti(SO_4)_2 + H_2O_2 + 2H_2O \longrightarrow H_2TiO_4 + 2H_2SO_4$$

Or

$$Ti^{4+} + H_2O_2 + 2H_2O \longrightarrow H_2TiO_4 + 4H^{\oplus}$$

$$H_2TiO_4 \longrightarrow TiO_3 + H_2O.$$

This reaction is used as a test of H_2O_2.

9. **Reaction with acidic solution of K_2CrO_4 or $K_2Cr_2O_7$:** On addition of H_2O_2 to a solution of K_2CrO_4 or $K_2Cr_2O_7$ containing dilute H_2SO_4 and small amount of ether, ethereal layer turns intense blue in colour. This is due to the formation of chromium diperoxide [or chromic peroxide], CrO_5 or $Cr(O_2)_2O$.

$$K_2CrO_4 + H_2SO_4 + 2H_2O_2 \xrightarrow{\text{Ether}} K_2SO_4 + CrO_5 + 3H_2O$$

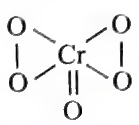
Or

$$CrO_4^{2-} + 2H^{\oplus} + 2H_2O_2 \xrightarrow{\text{Ether}} CrO_5 + 3H_2O$$

$$\underset{\text{Potassium dichromate}}{K_2Cr_2O_7} + H_2SO_4 + 2H_2O_2 \xrightarrow{\text{Ether}} K_2SO_4 + 2CrO_5 + 5H_2O$$

Or

$$Cr_2O_7^{2-} + 2H^{\oplus} + 4H_2O_2 \xrightarrow{\text{Ether}} 2CrO_5 + 5H_2O$$



Note: CrO_5 is known as butterfly structure.

This reaction is used as a test for H_2O_2.

10. **Reaction with alkenes:** H_2O_2 reacts with alkenes to form glycols. (addition reaction)

$$\underset{\text{Ethylene}}{H_2C=CH_2} + H_2O_2 \longrightarrow \underset{\text{Ethylene glycol}}{\underset{OH\ \ \ OH}{H_2C-CH_2}}$$

11. **Addition compounds:** Hydrogen peroxide forms addition compounds with certain inorganic salts, and few organic compounds.

For example, $Na_2HPO_4 \cdot H_2O_2$, $(NH_4)_2SO_4 \cdot H_2O_2$ and $Co(NH_2) \cdot H_2O_2$ (Trade name ortizon or hyperol). They give H_2O_2 on reacting with water.

3.9.6 Uses of H_2O_2

The uses of H_2O_2 are as follows:

1. H_2O_2 is used in the industries as a bleaching agent for textiles, paper, leather, straw, fats, oils etc.
2. Domestically, it is used as a hair bleach and as a mild disinfectant (for washing wounds, teeth and ears).
3. In laboratory, it is used as an oxidising agent.
4. H_2O_2 is extensively used to manufacture chemicals such as sodium perborate and percarbonate which are important constituents of high-quality detergents.
5. H_2O_2 is used for the production of epoxides, propylene oxide and polyurethans.
6. H_2O_2 is also used in the synthesis of hydroquinone, pharmaceuticals (cephalosporins), tartaric acid and few food products.
7. A fast growing use of H_2O_2 is in environmental (green) chemistry, for example:
   a. In the pollution control treatment of domestic and industrial effluents.
   b. Oxidation of cyanides.
   c. restoration of aerobic conditions to sewage wastes.
8. For restoring the colour of blackened lead paintings.
9. As a propellant or fuel in submarines and rockets.

3.9.7 Strength of H_2O_2 Solution

Strength or concentration of H_2O_2 solution is expressed in the following ways:

1. **In terms of volume of O_2 gas:** The volume (in mL) of O_2 gas produced at STP on heating one volume (or 1 mL) of H_2O_2 solution is known as the concentration of H_2O_2 solution. The commercial samples are marked as '10 volume', '20 volume', '30 volume', etc.
   a. 10 volume means that one volume of H_2O_2 solution on heating at STP produces 10 volume of O_2 gas or 1mL of H_2O_2 solution on heating at STP produces 10 mL of O_2 gas.

b. Similarly, 10 mL of 10 volume solution of H_2O_2 will give, $10 \times 10 = 100$ mL of O_2 gas at STP.

c. 10 mL of 20 volume solution of H_2O_2 will give $10 \times 20 = 200$ mL of O_2 gas at STP.

Thus the strength of 10 volume and 20 volume H_2O_2 solution is 10 mL and 20 mL respectively.

2. **In terms of percentage weight:** The weight of pure H_2O_2 in a given sample of H_2O_2 may be expressed in terms of percentage weight, i.e. g 100 mL^{-1} or g L^{-1}. Thus 5% H_2O_2 solution (w/v) means that 5 g of H_2O_2 is present in 100 mL of solution.

a. The concentration of a '10 volume' solution of H_2O_2 in terms of percentage weight and in g L^{-1} is 3.035% and 30.35 g L^{-1} respectively. This can be calculated as follows:

$$\underset{\substack{2(34)\text{ g}\\=68\text{ g}}}{2H_2O_2} \xrightarrow{\Delta} 2H_2O + \underset{\substack{32\text{ g at STP}\\\text{or }22400\text{ mL at STP}}}{O_2}$$

22400 mL of O_2 gas is obtained at NTP from 68 g of H_2O_2

$\therefore$ 10 mL of O_2 gas is obtained at NTP from

$$\frac{68}{22400} \times 10 \text{ g of } H_2O_2 = 0.03035 \text{ g of } H_2O_2$$

1 mL of H_2O_2 contains 0.03035 g of H_2O_2

100 mL of H_2O_2 contains $0.3035 \times 100 = 3.035$ g of H_2O_2

Hence, concentration of '10 volume' of H_2O_2 solution is 3.035% (w/v) or concentration or strength of '10 volume' of H_2O_2 solution is $3.035 \times 10 = 30.35$ g L^{-1}.

3. **In terms of normality:** To know the normality, equivalent weight of H_2O_2 should be known, and this can be calculated as follows:

$$\underset{\substack{(2\times 34)\\=68\text{ g}}}{2H_2O_2} \longrightarrow 2H_2O + \underset{32\text{ g}}{O_2}$$

32 parts by weight of O_2 are obtained from 68 parts by weight of H_2O_2

$\therefore$ 8 parts by weight of O_2 are obtained from $\frac{68 \times 8}{32}$

$= 17$ parts by weight of H_2O_2

$\therefore$ Equivalent weight of $H_2O_2 = 17$.

$$\boxed{1N = 17 \text{ gL}^{-1}}$$

Normality of 10 volume H_2O_2 solution

$$= \frac{\text{Strength of 10 volume } H_2O_2 \text{ soln in g } L^{-1}}{\text{Equivalent weight of } H_2O_2} = \frac{30.35}{17}$$

$= 1.785$ N

$$\underset{2\text{ mol}}{2H_2O_2} \longrightarrow 2H_2O + \underset{1\text{ mol}}{O_2}$$

2 mol of $H_2O_2 = 22.4$ L of O_2

1 mol of $H_2O_2 = 11.2$ L of O_2

1M $H_2O_2 \equiv 11.2$ L of O_2

1N $H_2O_2 \equiv 5.6$ L of $O_2 = 5.6$ volume of O_2

Alternatively:

$2H_2O_2 \longrightarrow 2H_2O + O_2$

2×34 $gL^{-1} \equiv 22.4$ L of O_2 at STP

17 $gL^{-1} \equiv 1N = 5.6$ g L of O_2

Alternatively:

$H_2O_2 \equiv O_2$

1 equivalent $\equiv$ equivalent $\left(\frac{22.4}{4} L = 5.6 L\right)$

$$\boxed{1.7\% \text{ of } H_2O_2 = 17 \text{ gL}^{-1} \text{ of } H_2O_2 \equiv 5.6 \text{ L of } O_2 = 8 \text{ g of } O_2}$$

(1L $\equiv$ 1000 mL of $H_2O_2 \equiv 17$ g of H_2O_2

100 mL of $H_2O_2 \equiv 1.7$ g of $H_2O_2 = 1.7\%$ of H_2O_2)

General formula of volume strength of H_2O_2

a. 1.7% of $H_2O_2 \equiv 17$ gL^{-1} of $H_2O_2 \equiv 5.6$ L of O_2 at STP $\equiv 8$ g of O_2 at STP

b. Volume strength of $H_2O_2 \times$ Volume of H_2O_2 = Volume of O_2 at STP

c. 3% solution of H_2O_2 is marked as 10 volume H_2O_2

d. 30% solution of H_2O_2 is marked as 100 volume H_2O_2

3.9.8 Use of Liquid Hydrogen as Fuel

Liquid hydrogen has already been used as rocket fuel. The chemical reaction involved is:

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)} + 286 \text{ kJ}$$

Both reactants H_2 and O_2 are stored as liquids in separate tanks. The hydrogen tank holds 1.5×10^6 L of liquid hydrogen. The oxygen tank carries 5.4×10^5 L of liquid oxygen. During the 'lift off' operations, these propellants power the shuttle's main engine for about 8.5 min. Here, liquid hydrogen is consumed at the rate of nearly 3000 L sec^{-1}.

Hydrazone or Triatomic hydrogen (H_3)

The existence of H_3 was proposed by J.J. Thomson (1920) in his experiments on cathode rays. It can be prepared by the action of X-rays from radium on ordinary hydrogen. It can also be prepared by passing silent electric discharge (app. 20,000 V) through ordinary hydrogen. The yield of H_3 is 0.02%

- H_3 is highly unstable having very short lifespan.
- H_3 rapidly changes into ordinary hydrogen and cannot be stored as such.

ILLUSTRATION 3.18

Calculate (a) normality, (b) molarity, (c) strength in gL^{-1} and (d) percentage strength of 10 volume H_2O_2.

Sol.

a. 5.6 volume strength of $H_2O_2 \equiv 1N$

10 volume strength of $H_2O_2 = \dfrac{10}{5.6}$ N = 1.785 N

b. Molarity

$$M = \frac{N}{n\text{-factor}} = \frac{1.785}{2} \quad (\because n\text{-factor of } H_2O_2 = 2)$$

$$= 0.89 \text{ M}$$

c. 5.6 volume strength of $H_2O_2 = 17$ g L^{-1}

10 volume strength of $H_2O_2 = \dfrac{17 \times 10}{5.6} = 30.35$ gL^{-1}

d. 5.6 volume strength of $H_2O_2 = 1.7\%$

10 volume strength of $H_2O_2 = \dfrac{1.7 \times 10}{5.6} = 3.03\%$

ILLUSTRATION 3.19

Calculate the number of moles and weight of O_2 produced on heating 1.12 L of 10 volume strength of H_2O_2 at STP.

Sol. Volume of O_2 at STP

= volume of H_2O_2 × volume strength of H_2O_2

= 1.12 L × 10 = 11.2 L

Moles of O_2 at STP $= \dfrac{11.2 \text{ L}}{22.4 \text{ L}} = 0.5$ mol

Weight of $O_2 = 0.5 \times 32 = 16.0$ g

ILLUSTRATION 3.20

10 ml of H_2O_2 liberates 12.7 g of iodine from an acidic KI solution. Calculate (a) normality, (b) molarity, (c) volume strength, (d) strength and (e) percentage strength of H_2O_2.

Sol.

a. MW $(I_2) = 2 \times 127 = 254$ g

EW $(I_2) = \dfrac{254}{2} = 127$ g

$(\because 2I^{\ominus} \longrightarrow I_2 + 2e^{\ominus}, n = 2)$

$H_2O_2 \equiv KI \equiv I_2$

1 mEq ≡ 1 mEq ≡ 1 mEq

$$N_1V_1 \text{ (mL)} = \frac{\text{Weight of } I_2}{\text{EW}(I_2)} \times 10^3 \text{ (mEq)}$$

$$N_1 \times 10 \text{ mL} = \frac{12.7 \times 10^3}{127}$$

N_1 of $H_2O_2 \equiv 10$N

b. Molarity of $H_2O_2 = \dfrac{N}{n\text{-factor}} = \dfrac{10}{2} = 5$ M

c. 1 N of H_2O_2 = 5.6 volume strength of H_2O_2

10 N of $H_2O_2 = 5.6 \times 10 = 56$ volume strength of H_2O_2

d. 1 N of $H_2O_2 = 17$ gL^{-1}

10 N of $H_2O_2 = 17 \times 10 = 170$ gL^{-1}

e. 1 N of $H_2O_2 = 1.7\%$

10 N of $H_2O_2 = 17\%$

ILLUSTRATION 3.21

A solution of $K_2Cr_2O_7$ containing 4.9 gL^{-1} is used to titrate H_2O_2 solution containing 3.4 gL^{-1} in acidic medium. What volume of $K_2Cr_2O_7$ will be required to react with 20 mL of H_2O_2 solution? Also calculate the strength of H_2O_2 in terms of available oxygen.

Sol. Strength = Normality × Equivalent weight = $N \times$ EW

$$\text{EW } (K_2Cr_2O_7) = \frac{39 \times 2 + 52 + 2 + 16 \times 7}{6} = \frac{294}{6} = 49.0 \text{ g}$$

$\because$ In acidic medium,

$Cr_2O_7^{2-} + 14H^{\oplus} + 6e^{\ominus} \longrightarrow 2Cr^{3+} + 7H_2O$, n-factor = 6

$$\text{N } (K_2Cr_2O_7) = \frac{\text{Strength}}{\text{EW}} = \frac{4.9}{49} = 0.1 \text{ N}$$

$$\text{N } (H_2O_2) = \frac{\text{Strength}}{\text{EW}} = \frac{3.4}{17} = 0.2 \text{ N}$$

$$\left\{\begin{array}{l} H_2O_2 \longrightarrow O_2 + 2H^{\oplus} + 2e^{\ominus} \quad (n = 2) \\ \text{EW} = \dfrac{34}{2} = 17 \text{ g} \end{array}\right\}$$

$Cr_2O_7^{2-} \equiv H_2O_2$

mEq of $Cr_2O_7^{2-} \equiv$ mEq of H_2O_2

$N_1V_1 = N_2V_2$

$0.1 \times V_1 = 0.2 \times 20$

$$V_1 = \frac{0.2 \times 20}{0.1} = 40 \text{ mL}$$

Volume strength of H_2O_2

1 N = 5.6 L of O_2 (Volume strength of H_2O_2)

0.2 N = 5.6 × 0.2 = 1.12 L of H_2O_2

It is written as 1.12 volume of H_2O_2.

ILLUSTRATION 3.22

When 100 mL of an aqueous solution of H_2O_2 is titrated with an excess of KI solution in dilute H_2O_2, the liberated I_2 required 50 mL of 0.1 M $Na_2S_2O_3$ solution for complete reaction. Calculate the percentage strength and volume strength of H_2O_2 solution.

Sol. Reactions involved are as follows:

$$2I^{\ominus} \longrightarrow I_2 + \cancel{2e^{\ominus}} \quad \text{...(i)}$$

$$2H^{\oplus} + \cancel{2e^{\ominus}} + H_2O_2 \longrightarrow 2H_2O \quad \text{...(ii)}$$

$$H_2O_2 + 2I^{\ominus} + 2H^{\oplus} \longrightarrow I_2 + H_2O \quad \text{...(iii)}$$

$$\cancel{2e^{\ominus}} + I_2 \longrightarrow 2I^{\ominus} \quad \text{...(iv)}$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + \cancel{2e^{\ominus}} \quad \text{...(v)}$$

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^{\ominus} \quad \text{...(vi)}$$

For Eq. (v), n-factor $= \frac{2}{2} = 1$

$$H_2O_2 \equiv I^{\ominus} \equiv I_2 \equiv S_2O_3^{2-}$$

mEq of $H_2O_2 \equiv$ mEq of $I^{\ominus} \equiv$ mEq of $I_2 \equiv$ mEq of $S_2O_3^{2-}$

$$N_1V_1 \text{ (mL)} \equiv N_2V_2 \text{ (mL)}$$

$$N_1 \times 100 \equiv 0.1 \times 1(n\text{-factor}) \times 50 \text{ mL}$$

$$N\,(H_2O_2) = \frac{0.1 \times 1 \times 50}{100} = 0.05 \text{ N}$$

$$1\text{N } H_2O_2 \equiv 1.7\% \text{ of } H_2O_2$$

$$0.05 \text{ N } H_2O_2 \equiv 1.7 \times 0.05 = 0.085\% \text{ of } H_2O_2$$

$$1 \text{ N } H_2O_2 \equiv 5.6 \text{ volume of } O_2$$

$$0.05 \text{ N } H_2O_2 = 5.6 \times 0.05 = 0.28 \text{ volume of } O_2$$

Volume strength of $H_2O_2 = 0.28$ volume

ILLUSTRATION 3.23

Calculate the volume strength of H_2O_2 solution if 50 mL of H_2O_2 solution is diluted with 50 mL of H_2O. 20 mL of this diluted solution required 40 mL of M/60 $K_2Cr_2O_7$ solution in presence of H_2SO_4 for complete reaction.

Sol. $H_2O_2 \equiv Cr_2O_7^{2-}$

$(n = 2) \quad (n = 6)$

$$\text{mEq} \equiv \text{mEq}$$

$$N_1V_1 \equiv N_2V_2$$

$$N_1 \times 20 \equiv \frac{1}{60} \times 6 \times 40$$

$$N_1 = \frac{6 \times 40}{60} = \frac{1}{20} = 0.2 \text{ N of 100 mL of } H_2O_2 \text{ on dilution}$$

The normality of the 50 mL of H_2O_2 should be twice the normality of 20 mL of the diluted solution of H_2O_2, since the volume of H_2O_2 solution has doubled.

(50 mL of H_2O_2 + 50 mL of H_2O = 100 mL of solution of H_2O_2)

$$\therefore\ N_1V_1 = N_2V_2$$

$$0.2 \times 100 \text{ mL} = N_2 \times 50 \text{ mL}$$

$$N_2 = 0.4\text{N}$$

$\therefore$ Volume strength of $H_2O_2 = 5.6 \times 0.4$
$= 2.24$ volume of O_2

ILLUSTRATION 3.24

50 mL of ozone, O_3 at STP was passed through 50 mL of '5 volume' H_2O_2 solution. What is the volume strength of H_2O_2 after the reaction?

Sol. $O_3 \longrightarrow O_2 + O$ ...(i)

$H_2O_2 \longrightarrow H_2O + O$ ...(ii)

$O + O \longrightarrow O_2$ ...(iii)

(½ vol) (½ vol) (1 vol)

From Eqs. (i) and (ii), we get 50 mL of O_3 at STP will produce 50 mL of molecular O_2 as such and 50 mL of oxygen molecule after reaction with H_2O_2.

This new volume of 50 mL of molecular oxygen after reaction with H_2O_2 is contributed equally by O_3 and H_2O_2. Thus, 25 mL of oxygen has been contributed by H_2O_2,

Volume of H_2O_2 × volume strength of H_2O_2
= Volume of O_2 at STP

50 mL × 5V H_2O_2 = 250 mL of O_2 at STP.

After utilisation of 25 mL of O_2, according to Eq. (iii), the balance (250 – 25) mL = 225 mL of O_2 is still available by 50 mL of H_2O_2.

Hence, volume strength of H_2O_2, after reaction is

$$\frac{\text{Volume of } O_2 \text{ at STP}}{\text{Volume of } H_2O_2} = \frac{225}{50} = 4.5$$

$\therefore$ Volume strength = 4.5

ILLUSTRATION 3.25

5.1 g sample of H_2O_2 solution containing x% H_2O_2 by weight requires x mL of $K_2Cr_2O_7$ solution for complete oxidation under acidic condition. What is the molarity of $K_2Cr_2O_7$ solution?

Sol. 100 g of H_2O_2 solution contains = x g of H_2O_2

$$5.1 \text{ g of } H_2O_2 \text{ solution contains} = \frac{x \times 5.1}{100} \text{ g of } H_2O_2$$

$$= \text{Weight of } H_2O_2$$

$$\text{mEq of } H_2O_2 = \frac{\text{Weight of } H_2O_2 \times 10^3}{\text{EW } (H_2O_2)}$$

$$= \frac{5.1x}{100} \times 10^3 \times \frac{1}{17} = 3x \text{ mEq}$$

$$\because\ Cr_2O_7^{2-} \equiv H_2O_2$$

$$\text{mEq} \equiv \text{mEq}$$

$$N_1V_1 = 3x$$

$$N_1 \times x = 3x$$

$$N(K_2Cr_2O_7) = 3 \text{ N}$$

$$M\,(K_2Cr_2O_7) = \frac{N}{n} = \frac{3}{6} = 0.5 \text{ M}$$

ILLUSTRATION 3.26

200 mL of acidified 3 N H_2O_2 is reacted with $KMnO_4$ solution till there is a light tinge of purple colour. Calculate the volume of O_2 produced at STP.

Sol. N of H_2O_2 = 5.6 volume of O_2

3 N of $H_2O_2 = 3 \times 5.6 = 16.8$ volume of O_2 (volume strength of H_2O_2)

Volume of O_2 produced by H_2O_2 at STP
= Volume of O_2 × Volume strength of H_2O_2
= 200 mL × 16.8 = 3360 mL

Same volume will be produced by $KMnO_4$ = 3360 mL

Total volume of O_2 produced = 3360 + 3360 = 6720 mL
= 6.72 L

ILLUSTRATION 3.27

a. When H_2O_2 is added to blood, rapid evolution of a gas occurs. Why?

b. Hydrogen peroxide acts both as an oxidising and as a reducing agent in alkaline solution towards certain first row transition metal ions. Illustrate both these properties of H_2O_2 using chemical equations.

Sol.

a. The enzyme present in the blood catalyses the oxidation of H_2O_2 and hence rapid evolution of O_2 takes place.

$$2\,H_2O_2 \xrightarrow[\text{(in blood)}]{\text{Enzyme}} 2H_2O + O_2\uparrow$$

b. As oxidising agent in basic medium: Chromium hydroxide is oxidized by H_2O_2 in presence of NaOH into sodium chromate.

$$[H_2O_2 \longrightarrow H_2O + [O]] \times 3$$
$$2Cr(OH)_3 + NaOH + 3[O] \longrightarrow 2Na_2CrO_4 + 5H_2O$$
$$\overline{2Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O}$$

ILLUSTRATION 3.28

What happens when:

a. Chromium hydrogen is treated with hydrogen peroxide in the presence of sodium hydroxide.

b. Hydrogen peroxide is added to ferrous ammonium sulphate solution.

c. Hydrogen peroxide is added to acidified potassium permanganate.

d. An alkaline solution of potassium ferricyanide is reacted with H_2O_2.

Sol.

a. Chromium hydroxide is converted into soluble yellow sodium chromate.

$$[H_2O_2 \longrightarrow H_2O + [O]] \times 3$$
$$Cr(OH)_3 + 4NaOH + 3[O] \longrightarrow 2Na_2CrO_4 + 5H_2O$$
$$\overline{2Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O}$$

b. Ferrous ammonium sulphate is oxidised to ferric salt.

$$H_2O_2 \longrightarrow H_2O + [O]$$
$$[O] + 2FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O$$
$$\overline{2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O}$$

c. Potassium permanganate is decolourised.

$$2KMnO_4 + H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$[H_2O_2 + [O] \longrightarrow H_2O + O_2] \times 5$$
$$\overline{2\,KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5H_2O}$$

d. Potassium ferricyanide is reduced to potassium ferrocyanide.

$$2K_3[Fe(CN)_6] + 2KOH \longrightarrow 2K_4[Fe(CN)_6] + H_2O + [O]$$
$$H_2O_2 + [O] \longrightarrow H_2O + O_2$$
$$\overline{2K_3[Fe(CN)_6] + 2KOH + H_2O_2 \longrightarrow 2K_4[Fe(CN)_6] + 2H_2O + O_2}$$

ILLUSTRATION 3.29

There are three samples of H_2O_2 labelled as 10 vol, 15 vol, 20 vol. Half litres of each sample are mixed and then diluted with equal volume of water. Calculate the volume strength of resultant solution.

Sol. Volume strength = 5.6 × Normality

Or

$$V = 5.6 \times N, \text{ Total volume} = \left(\frac{1}{2}+\frac{1}{2}+\frac{1}{2}\right)+\frac{3}{2} = 3L$$

$$N_1 = \frac{10}{5.6}, N_2 = \frac{15}{5.6}, N_3 = \frac{20}{5.6}$$

$$N_1V_1 + N_2V_2 + N_3V_3 = N_RV_R$$

$$\frac{10}{5.6}\times\frac{1}{2}+\frac{15}{5.6}\times\frac{1}{2}+\frac{20}{5.6}\times\frac{1}{2} = N_R \times 3L$$

$$\Rightarrow N_R = 1.339$$

$$\text{Volume strength} = N_R \times 5.6$$
$$= 1.339 \times 5.6 = 7.5$$

CONCEPT APPLICATION EXERCISE 3.2

1. What do you understand by 'Water gas shift reaction'? Discuss its use for the preparation of hydrogen.
2. Hydrogen forms compounds with elements having atomic numbers: 9, 11, 12 and 17. What are their chemical formulas? Compare their chemical behaviour.
3. What are metallic/interstitial hydrides? How do they differ from molecular hydrides?
4. Complete the following reactions:
   - **a.** $CaO_{(s)} + H_2O_{(1)} \rightarrow$
   - **b.** $Na_2O_{(s)} + H_2O_{(1)} \rightarrow$
5. Explain why hydrogen peroxide is stored in coloured plastic bottles?
6. Describe the industrial applications of hydrogen dependent on:
   - **a.** the heat liberated when its atoms are made to combine on the surface of a metal.
   - **b.** its effect on unsaturated organic systems in presence of a catalyst.
   - **c.** its ability to combine with nitrogen under specific conditions.
7. How is dihydrogen prepared
   - **a.** from water by using a reducing agent?
   - **b.** in the laboratory in pure form?
   - **c.** from hydrocarbons?
8. Complete the following:
   - **a.** $Fe_{(s)} + H_2O_{(g)} \rightarrow$
   - **b.** $PbS_{(s)} + H_2O_{2(aq)} \rightarrow$
   - **c.** $MnO_{4\,(aq)}^{\ominus} + H_2O_{2(aq)} \rightarrow$
9. Discuss the importance of heavy water in nuclear reactors.
10. How is heavy water prepared from normal water?

11. Explain why water has high boiling and melting points as compared to H_2S.
12. Distinguish between:
   a. Hard water and soft water
   b. Temporary hardness and permanent hardness
13. Explain the correct context in which the following terms are used:
   a. Diprotium   b. Dihydrogen
   c. Proton   d. Hydron
14. Is it correct to say that hydrogen can behave as a metal? State the conditions under which such behaviour can be possible.
15. Name the isotopes of hydrogen. What is the importance of the heavier isotopes of hydrogen?
16. How many allotropes of dihydrogen are known? What is their importance?
17. Name the class of hydrides to which H_2O, B_2H_6, NaH and LaH_3 belong. What is understood by 'hydride gap'?
18. Hydrogen forms three types of bonds in its compounds. Describe each type of bonding using suitable examples.
19. Elements with atomic numbers 17 and 20 form compounds with hydrogen. Write the formula of these two compounds and compare their chemical behaviour in water.
20. Complete the following reactions:
   a. $CuO_{(s)} + H_{2(g)} \rightarrow$
   b. $CO_{(g)} + H_{2(g)} \rightarrow$
21. Describe some unusual properties of water.
22. What is the difference between hydrolysis and hydration?
23. What is understood by hydrogenation?
24. What are the advantages in using hydrogen as a fuel?
25. Ionic hydrides are frequently used to remove traces of water from organic compounds. What is the underlying basis of this process?
26. Although D_2O resembles H_2O chemically yet it is a toxic substance. Explain.
27. Why do lakes freeze from water top towards bottom?
28. Why is ice dense than water and what kind of attractive forces must be overcome to melt ice?
29. A white solid is either Na_2O or Na_2O_2. A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid.
   a. Identify the substance and explain with balanced equation.
   b. Explain what would happen to the red litmus if the white solid were the other compound.
30. Explain the following:
   a. Hydrated barium peroxide is used in the preparation of H_2O_2 instead of anhydrous barium peroxide.
   b. Phosphoric acid is preferred to sulphuric acid in the preparation of H_2O_2 from barium peroxide.
   c. Hydrogen is not prepared by action of concentrated sulphuric acid on zinc.
   d. A solution of ferric chloride is unaffected when hydrogen is bubbled through it, but gets reduced when zinc is added to the same acidified solution.
31. An element has the minimum and maximum oxidation states as –X and +X respectively. It does not have the possibility of undergoing disproportionation in any of its compounds. What is the value of X ?
32. Give reason for the following:
   a. The process $\frac{1}{2}H_{2(g)} + e^{\ominus} \longrightarrow H^{\ominus}_{(g)}$ is endothermic, yet ionic hydrides are known.
   b. A mixture of hydrazine and H_2O_2 with Cu(II) catalyst is used as a rocket propellant.
   c. It is possible to remove completely the temporary hardness caused due to $Mg(HCO_3)_2$ by boiling.
33. The degree of hardness of a given sample of hard water is 40 ppm. If the entire hardness is due to $MgSO_4$, how much of $MgSO_4$ is present per kg of water?

Solved Examples

EXAMPLE 3.1

A 5.0 mL of solution of H_2O_2 liberates 0.508 g of iodine from acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at STP.

Sol. mEq of $I_2 = \dfrac{0.508}{127} \times 1000$

mEq of KI $= \dfrac{0.508}{127} \times 1000$

mEq of $H_2O_2 = \dfrac{0.508}{127} \times 1000$

Normality of $H_2O_2 = \dfrac{0.503}{127} \times \dfrac{1000}{5}$

For H_2O_2,

5.6 × Normality = Volume strength

$\therefore$ Volume strength $= 5.6 \times \dfrac{0.508 \times 1000}{127 \times 5}$

$= 4.48$V

EXAMPLE 3.2

To a 25 mL H_2O_2 solution, excess of an acidified solution of potassium iodine was added. The iodine liberated required 20 mL of 0.3 N sodium thiosulphate solution. Calculate the volume strength of H_2O_2 solution.

Sol. mEq of $Na_2S_2O_3 = 20 \times 0.3 = 6$

mEq of $I_2 = 6$

mEq of $H_2O_2 = 6$

$$\text{Normality of } H_2O_2 = \frac{6}{25}$$

For H_2O_2, 5.6 × Normality = Volume strength

$$\therefore \text{ Volume strength} = 5.6 \times \frac{6}{25} = 1.344$$

EXAMPLE 3.3

Element (A) burns in nitrogen to give an ionic compound, (B) reacts with water to give (C) and (D). A solution of (C) becomes milky on bubbling carbon dioxide. Identify (A), (B), (C) and (D).

Sol.

a. Since element (A) burns in nitrogen to give an ionic compound, therefore (B) must be a metal nitride

b. Since (B), a metal nitride reacts with water, (B) is ionic nitride and the product formed, i.e. (C) and (D) are metal hydroxides and ammonia, (NH_3).

c. Since (C) becomes milky on bubbling CO_2, (C) must by calcium hydroxide, $Ca(OH)_2$.

All reactions involved in the question can be explained as follows:

$$\underset{(A)}{3Ca_{(s)}} + N_{2(g)} \xrightarrow{\Delta} \underset{\substack{\text{Calcium nitride}\\(B)}}{Ca_3N_{2\,(s)}}$$

$$\underset{(B)}{Ca_3N_2} + 6H_2O \longrightarrow \underset{\substack{\text{Calcium}\\\text{hydroxide(C)}}}{Ca(OH)_2} + \underset{\text{Ammonia (D)}}{2NH_{3\,(g)}}$$

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\substack{\text{Calcium}\\\text{carbonate}\\\text{(milkiness)}\\(D)}}{CaCO_3\downarrow} + H_2O$$

Thus, (A) = Ca, (B) = Ca_3N_2, (C) = $Ca(OH)_2$ (D) = NH_3

EXAMPLE 3.4

Calculate the volume of 10 volume H_2O_2 solution that will react with 200 mL of 2 N $KMnO_4$ in acidic medium.

Sol. Normality of 10 volume $H_2O_2 = \dfrac{\text{Volume strength}}{5.6} = \dfrac{10}{5.6}$ N

Applying normality equation,

$$\underset{(H_2O_2)}{N_1V_1} = \underset{(KMnO_4)}{N_2V_2}$$

$$\frac{10}{5.6} \times V_1 = 2 \times 200$$

$$V_1 = \frac{2 \times 200 \times 5.6}{10} = 224 \text{ mL}$$

EXAMPLE 3.5

An aqueous compound of an inorganic compound (X) shows the following reactions:

a. It decolourises an acidified $KMnO_4$ solution accompanied by the evolution of oxygen.

b. It liberates I_2 from an acidified KI solution.

c. It gives a brown precipitate with alkaline $KMnO_4$ solution with evolution of oxygen.

d. It removes black stains from old oil paintings.

Identify (X) and give chemical equations for the reactions at steps (a) to (d).

Sol. In reactions (a) and (c), (X) acts as a reducing agent, while in (b), it acts as an oxidising agent. Thus these reactions indicate that (X) is H_2O_2 which is further confirmed from reaction (d).

a. $$\underset{\substack{\text{Purple}\\\text{coloured}}}{2KMnO_4} + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + \underset{\text{Colourless}}{2MnSO_4} + 8H_2O + 5O_2$$

b. $$2KI + H_2SO_4 + H_2O_2 \longrightarrow K_2SO_4 + I_2 + 2H_2O$$

c. $$2KMnO_4 + 3H_2O_2 \longrightarrow 2KOH + \underset{\text{Brown}}{2MnO_2} + 2H_2O + 3O_2$$

d. $$\underset{\text{Black}}{PbS} + 4H_2O_2 \longrightarrow \underset{\text{White}}{PbSO_4} + 4H_2O$$

EXAMPLE 3.6

3.4 g sample of H_2O_2 solution containing x% H_2O_2 by weight requires x mL of a $KMnO_4$ solution for complete oxidation under acidic condition. The normality of $KMnO_4$ solution is:

a. 1 N   b. 2 N   c. 3 N   d. 0.5 N

Sol. 100 g of H_2O_2 sample contains = 'x' g H_2O_2

3.4 g of H_2O_2 sample solution contains = $\dfrac{x}{100} \times 3.4$ g

$$\text{Weight of } H_2O_2 = \frac{3.4x}{100}$$

$$\text{Eq of } H_2O_2 = \frac{3.4x}{100} \times \frac{1}{17}$$

$$\text{mEq of } H_2O_2 = \frac{3.4x}{100 \times 17} \times 1000 = \frac{34x}{17} = 2x$$

mEq of $KMnO_4 = x \times N$

$\therefore \quad x \times N = 2x$

$N = 2$

Hence, the correct option is (b).

EXAMPLE 3.7

If 100 mL of acidified 2N H_2O_2 is allowed to react with $KMnO_4$ solution till there is light tinge of purple colour, the volume of oxygen produced at STP is:

a. 2.24 L   b. 1.12 L   c. 3.36 L   d. 4.48 L

Sol. Volume of O_2 at STP = 100 mL × 11.2 volume strength
= 1120 mL of O_2 at STP

(Since 1N = 5.6 volume strength; 2N = 11.2 volume strength of H_2O_2)

Volume of O_2 produced by H_2O_2 = 1120 mL

Same volume of O_2 produced by $KMnO_4$ = 1120 mL

Total volume of $O_2 = 2240$ mL $= 2.24$ L

Hence, the correct option is (a).

EXAMPLE 3.8

Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce a gas (A) and alkaline solution. The solution on exposure to air produces a thin solid layer of (B) on the surface. Identify the compounds (A) and (B).

Sol. $Ca + N_2 \xrightarrow{\Delta}$ white powder

$$\downarrow H_2O$$

Gas (A) + alkaline solution

$$\downarrow \text{air}$$

thin solid layer (B)

Ca on heating with N_2 produces calcium nitride, Ca_3N_2, a white powder. Ca_3N_2 on reacting with water produces ammonia gas (NH_3), i.e. (A) and alkaline solution, $Ca(OH)_2$. $Ca(OH)_2$ on exposure to air, reacts with atmospheric CO_2 to give insoluble $CaCO_3$.

Hence, (A) = NH_3, (B) = $CaCO_3$.

$$3Ca + N_2 \xrightarrow{\Delta} Ca_3N_2$$

$$Ca_3N_2 + 6H_2O \longrightarrow \underset{\substack{\text{Calcium}\\\text{hydroxide}\\\text{(alkaline solution)}}}{3Ca(OH)_2} + \underset{(A)}{2NH_3}$$

$$Ca(OH)_2 + \underset{(air)}{CO_2} \longrightarrow \underset{(B)}{CaCO_3\downarrow} + H_2O$$

Exercises

Single Correct Answer Type

Hydrogen and Hydrides

1. Which of the following process uses water gas shift reaction?
   (1) Merck's process (2) Lane's process
   (3) Permutit process (4) Bosch's process

2. In which of the following compound does hydrogen exhibit a negative oxidation state:
   (1) LiH (2) H_2O
   (3) HCl (4) none of these

3. The number of neutrons in deuterium is
   (1) 2 (2) 3
   (3) 1 (4) 0

4. In which of the following reaction dihydron acts as an oxidising agent?
   (1) $Ca + H_2 \longrightarrow CaH_2$ (2) $2H_2 + O_2 \longrightarrow 2H_2O$
   (3) $H_2 + F_2 \longrightarrow 2HF$ (4) $CuO + H_2 \longrightarrow Cu + H_2O$

5. Which of the following metal does not produce dihydrogen gas with dilute hydrochloric acid?
   (1) Mg (2) Zn
   (3) Ag (4) Ba

6. Which oxide cannot be reduced by H_2?
   (1) Al_2O_3 (2) CuO
   (3) ZnO (4) All of these

7. Ortho- and para-hydrogen differ in
   (1) atomic number
   (2) mass number
   (3) electron spin in two atoms
   (4) nuclear spin in two atoms

8. Nascent hydrogen consists of
   (1) hydrogen ions in the excited state
   (2) hydrogen molecules with excess energy
   (3) solvated protons
   (4) hydrogen atoms with excess energy

9. The hydride ion $H^{\ominus}$ is a stronger base than hydroxide ion. Which of the following reaction would occur if NaH is dissolved in water
   (1) $H^{\ominus}_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^{\oplus}_{(aq)}$
   (2) $H^{\ominus}_{(aq)} + H_2O_{(l)} \longrightarrow \overset{\ominus}{O}H_{(aq)} + H_2$
   (3) $H^{\ominus} + H_2O \longrightarrow$ No reaction
   (4) none of the above

10. Which of the following pair of substances will not evolve H_2 gas
    (1) Iron and aqueous H_2SO_4 (2) Copper and $HCl_{(aq)}$
    (3) Sodium and ethanol (4) Iron and steam

11. H_2 molecule has two electrons and two nuclei. In which form of hydrogen the spin of electrons and also the spin of nuclei are in opposite directions.
    (1) orthohydrogen (2) parahydrogen
    (3) metahydrogen (4) β-hydrogen

12. What is false about Lane's process?
    (1) Method is used for manufacture of dihydrogen
    (2) It involves the oxidation of iron by steam
    (3) It involves the reduction of $H_2O_{(g)}$ by iron
    (4) It involves the oxidation of water gas

13. Which of the following hydrides are generally non-stoichiometric in nature?
    (1) Ionic hydrogen (2) Molecular hydrides
    (3) Interstitial hydrides (4) All of these

14. Dihydrogen gas may be prepared by heating caustic soda on
    (1) Cu (2) Zn
    (3) Na (4) Ag

15. Hydrogen can react with the following even in dark:
    (1) I_2 (2) Cl_2
    (3) F_2 (4) Br_2

16. Hydrogen has the tendency to gain one electron to acquire helium configuration, in this respect, it resembles:
    (1) alkali metals (2) carbon
    (3) alkaline earth metals (4) halogens

17. Which of the following is used as rocket fuel?
    (1) Liquid O_2 (2) Liquid NH_3
    (3) Liquid N_2 (4) Liquid H_2

18. On burning hydrogen in air the colour of flame is
    (1) green (2) light bluish
    (3) yellow (4) none of these

19. When electric current is passed through an ionic hydride in molten state:
    (1) hydrogen is liberated at anode
    (2) hydrogen is liberated at cathode
    (3) hydride ion migrates towards cathode
    (4) hydride ion remains in solution

20. Among CaH_2, NH_3, NaH and B_2H_6 which are covalent hydrides?
    (1) NH_3 and B_2H_6 (2) NaH and CaH_2
    (3) NaH and NH_3 (4) CaH_2 and B_2H_6

21. Which of the following is correct for hydrogen?
    (1) It can form bonds in +1 as well as –1 oxidation state.
    (2) It is collected at cathode.
    (3) It has a very high ionisation potential.
    (4) All of the above

22. Hydrogen can be placed in group 17 of the periodic table because
    (1) hydrogen forms hydrides like NaH
    (2) hydrogen has isotopes D and T

(3) it is light
(4) hydrogen combines with halogens

23. Consider LiH, MgH_2 and CuH:
(1) all are ionic hydrides
(2) LiH, MgH_2 are ionic, whereas CuH is covalent
(3) all are covalent
(4) LiH is ionic, MgH_2 is covalent and CuH is metallic

24. Select the incorrect statement
(1) Bosch method for the preparation of $H_2(g)$ involves coal gasification followed by water-gas shift reaction
(2) Group 7 to 9 elements are referred as hydrogen gap elements
(3) Metallic hydrides are known as non-stoichiometric hydrides
(4) Cu dissolves in dil. H_2SO_4 and gives $H_2(g)$

25. Select the incorrect statements
(1) Ortho hydrogen has more thermal conductivity than para hydrogen
(2) Ionic hydride ion ($H^{\ominus}$) is a strong Lewis base and thus it reacts H_2O easily
(3) Ionic hydrides are used to remove traces of water from organic compounds
(4) In the conversion of atomic hydrogen into ordinary hydrogen, bond formation is exothermic

26. Select the incorrect statement
(1) The basic property of H_2 that it can be converted into liquid by cooling under pressure is useful for hydrogen economy
(2) From the study of isotopes of H_2 molecules, eight different types of hydrogen molecules are possible.
(3) Density of ionic hydrides is greater than metals from which they are formed.
(4) MgH_2 and CuH are intermediate hydrides

27. Select the incorrect statement
(1) Occlusion is shown by covalent hydrides
(2) Complex hydrides are good reducing agents
(3) Polymeric hydrides are stable upto 525 K and above this temperature they evolve $H_2(g)$
(4) In solid state NaH does not conduct electricity but on electrolysis of molten state of NaH, Na is formed at cathode and H_2 is evolved at anode.

Water

28. Which of the following represents the heavy water?
(1) water at 277 K
(2) water containing large contamination of lead salts
(3) deuterium oxide
(4) protium oxide

29. Hardness of water is due to dissolved impurities of
(1) calcium and magnesium salts
(2) barium and magnesium salts
(3) calcium and strontium salts
(4) sodium and potassium salts

30. When water is dropped over sodium peroxide, the colourless gas produced is
(1) dinitrogen (2) dioxygen
(3) dihydrogen (4) hydrogen peroxide

31. When a sample of hard water is passed through the layer of sodium zeolite resulting which of the following ions will not be present in the resulting sample of water obtained?
(1) Mg^{2+} and Ca^{2+} (2) Ca^{2+} and $Na^{\oplus}$
(3) Mg^{2+} and CO_3^{2-} (4) CO_3^{2-} and $Cl^{\ominus}$

32. One part of heavy water is present in X parts of ordinary water. Here X is
(1) 10 (2) 60
(3) 6000 (4) 600000

33. When zeolite, which is hydrated sodium aluminium silicate is treated with hard water, the sodium ions ($Na^{\oplus}$) are exchanged with
(1) $H^{\oplus}$ ions (2) Ca^{2+} ions
(3) SO_4^{2-} ions (4) $\overset{\ominus}{O}H$ ions

34. 10 L of hard water required 0.56 g of lime (CaO) for removing hardness. Hence, temporary hardness in ppm (part per million, 10^6) of $CaCO_3$ is
(1) 100 (2) 200
(3) 10 (4) 20

35. Heavy water is qualified as heavy liquid as it is.
(1) a heavy liquid
(2) an oxide of heavier isotope of oxygen
(3) an oxide of deuterium
(4) denser than water

36. Number of H-bonds formed by a water molecule is:
(1) 2 (2) 8
(3) 1 (4) 4

37. Surface water contains.
(1) suspended impurities (2) organic impurities
(3) salt (4) salt and organic compound

38. Which of the following is not a water softener?
(1) Calgon (2) Permutit
(3) Na_2SO_4 (4) Na_2CO_3

39. Calgon is an industrial name given to
(1) normal sodium phosphate
(2) sodium meta-aluminate
(3) sodium hexametaphosphate
(4) hydrated sodium aluminium silicate

40. Both temporary and permanent hardness is removed on boiling with
(1) $Ca(OH)_2$ (2) Na_2CO_3
(3) $CaCO_3$ (4) CaO

41. The exhausted permutit is generally regenerated by percolating through it a solution of
(1) sodium chloride (2) calcium chloride
(3) magnesium chloride (4) barium chloride

42. Heavy water is
(1) H_2O
(2) D_2O
(3) Water at 4°C
(4) water obtained by repeated distillation

43. The shape of water molecule is same as that of
(1) C_2H_2 (2) CO_2
(3) NH_3 (4) Cl_2O

44. Given colourless liquid will be determined whether it is water or not?
(1) By smelling
(2) By tasting
(3) By phenolphthalein
(4) By adding a pinch of anhydrous $CuSO_4$

45. Heavy water is used in atomic reactor as
(1) coolant
(2) moderator
(3) both coolant and moderator
(4) neither coolant nor moderator

46. Water softening by Clarke's process uses
(1) calcium bicarbonate (2) calcium hydroxide
(3) potash alum (4) sodium bicarbonate

47. Hard water is not fit for washing clothes because
(1) it contains Na_2SO_4 and KCl
(2) it gives precipitate
(3) it contains impurities
(4) it is acidic in nature

48. Select the correct statement.
(1) Melting point of H_2O is greater than that of D_2O
(2) The presence of H_2O can be detected by using anhydrous $CoCl_2$
(3) Marine species can survive in distilled water
(4) A sample of hard water is passed through the cation exchange resin, will not produce lather with soap.

49. Select the incorrect statement
(1) Permanent hardness is due to soluble sulphates, chlorides and nitrates of Ca and Mg
(2) Hardness of water depends on the soap consuming power
(3) Bond energy of covalent (O–H) bond in water is greater than bond energy of hydrogen bond
(4) K and KO_2 on reaction with H_2O will produce the same gaseous product

Hydrogen peroxide

50. Ethylene and H_2O_2 react to give
(1) CO_2, H_2O (2) CO, H_2O
(3) Ethylene oxide (4) Ethylene glycol

51. H_2O_2 cannot act as
(1) oxidising agent (2) dehydrating agent
(3) reducing agent (4) acid

52. H_2O_2 is reduced by
(1) O_3
(2) acidic $KMnO_4$ solution
(3) lead sulphide suspension in water
(4) none of these

53. 30-volume hydrogen peroxide means
(1) 30% of H_2O_2 by volume
(2) 30 g of H_2O_2 solution contains 1 g of H_2O
(3) 1 cm^3 of solution liberates 30 cm^3 of dioxygen gas at STP
(4) 30 cm^3 of the solution contains one mole of H_2O_2

54. The compound which gives H_2O_2 on treatment with dilute acid is
(1) PbO_2 (2) MnO_2
(3) TiO_2 (4) KO_2

55. Hydrolysis of one mole of peroxodisulphuric acid produces
(1) two moles of sulphuric acid and hydrogen peroxide
(2) two moles of peroxomonosulphuric acid
(3) one mole of sulphuric acid, one mole of peroxomonosulphuric acid and one mole of hydrogen peroxide
(4) one mole of sulphuric acid and one mole of peroxomonosulphuric acid

56. Barium peroxide reacts with phosphoric acid to produce barium phosphate alongwith
(1) water (2) hydrogen peroxide
(3) dioxygen (4) phosphine

57. The volume strength of 1.5 N H_2O_2 solution is
(1) 4.8 (2) 5.2
(3) 8.8 (4) 8.4

58. The volume of 10 volume H_2O_2 required to liberate 500 mL of O_2 at STP is
(1) 25 mL (2) 50 mL
(3) 100 mL (4) 125 mL

59. Pure H_2O_2 is
(1) semi-solid (2) liquid
(3) solid (4) gas

60. 34 g of H_2O_2 is present in 1120 mL of solution. This solution is called
(1) 10 vol solution (2) 20 vol solution
(3) 34 vol solution (4) 32 vol solution

61. A 5.0 mL solution of H_2O_2 liberates 1.27 g of iodine from an acidified KI solution. The percentage strength of H_2O_2 is
(1) 11.2 (2) 5.6
(3) 1.7 (4) 3.4

62. In Question 61, the strength of H_2O_2 in terms of volume strength is
(1) 11.2 (2) 5.6
(3) 1.7 (4) 3.4

63. 100 mL of ozone at STP was passed through 100 mL of 10 volume H_2O_2 solution. What is the volume strength of H_2O_2 after the reaction?
(1) 9.5 (2) 9.0
(3) 4.75 (4) 4.5

64. 25 mL samples of distilled water, tap water and boiled water required, respectively, 1 mL, 13 mL and 5 mL of soap solution to form a permanent lather. The ratio of temporary to permanent hardness in the tap water is
(1) 3:2 (2) 2:3
(3) 1:2 (4) 2:1

65. 3.4 g sample of H_2O_2 solution containing x% H_2O_2 by weight requires x mL of a $KMnO_4$ solution for complete oxidation under acidic condition. The normality of $KMnO_4$ solution is
(1) 1N (2) 2N
(3) 3N (4) 0.5N

66. If 100 mL of acidified 2 N H_2O_2 is allowed to react with $KMnO_4$ solution till there is a light tinge of purple colour. The volume of oxygen produced at STP is
(1) 2.24 L (2) 1.12 L
(3) 3.36 L (4) 4.48 L

67. 100 mL of 0.01 M $KMnO_4$ oxidises 100 mL H_2O_2 in acidic medium. Volume of the same $KMnO_4$ required in alkaline medium to oxidise 100 mL of the same H_2O_2 will be ($MnO_4^{\ominus}$ changes to Mn^{2+} in acidic medium and to MnO_2 in alkaline medium)
(1) $\frac{100}{3}$ mL (2) $\frac{500}{3}$ mL
(3) $\frac{300}{5}$ mL (4) None

68. 10 mL of H_2O_2 solution (volume strength = x) requires 10 mL of N/0.56 $MnO_4^{\ominus}$ solution in acidic medium. Hence x is
(1) 0.56 (2) 5.6
(3) 0.1 (4) 10

69. The normality and volume strength of a solution made by mixing 1.0 L each of 5.6 volume and 11.2 volume H_2O_2 solution are:
(1) 1N, 5.6 vol (2) 1.5 N, 5.6 vol
(3) 1.5N, 8.4 vol (4) 1N, 8.4 vol

70. 100 mL of H_2O_2 is oxidised by 100 mL of 0.01 M $KMnO_4$ in acidic medium ($MnO_4^{\ominus}$ reduced to Mn^{2+}). 100 mL of the same H_2O_2 is oxidised by V mL of 0.01 M $KMnO_4$ in basic medium. Hence V is
(1) 500 (2) 100
(3) $\frac{100}{3}$ (4) $\frac{500}{3}$

71. The purity of H_2O_2 in a given sample is 85%. Calculate the weight of impure sample of H_2O_2 which requires 10 mL of M/5 $KMnO_4$ solution in a titration in acidic medium
(1) 2 g (2) 0.2 g
(3) 0.17 g (4) 0.15 g

72. Which is false about H_2O_2?
(1) Acts both as an oxidising and reducing agent.
(2) Two –OH bonds lie in the same plane.
(3) Pale blue liquid.
(4) Can be oxidised by O_3

73. The oxygen atoms in H_2O_2 undergoes__hybridisation.
(1) sp^3 (2) sp^2
(3) sp (4) sp^3d^2

74. An orange coloured solution acidified with H_2SO_4 and treated with a substance 'X' gives a blue coloured solution of CrO_5. The substance 'X' is
(1) H_2O_2 (2) H_2O
(3) dil HCl (4) conc HCl

75. Hydrogen peroxide was first time prepared by
(1) Gay–Lussac (2) Priestley
(3) Thenard (4) Bernard

76. H_2O_2 is a
(1) monobasic acid (2) dibasic acid
(3) neutral (4) weak alkali

77. Which one of the following compounds is a peroxide?
(1) KO_2 (2) BaO_2
(3) MnO_2 (4) NO_2

78. 34 g of H_2O_2 is present in H_2O mL of solution. This solution is called:
(1) 10 vol (2) 20 vol
(3) 34 vol (4) 32 vol

79. A 5.0 cm^3 solution of H_2O_2 liberates 1.27 g of iodine from an acidified KI solution. The percentage strength of H_2O_2 is
(1) 11.2 (2) 5.6
(3) 1.7 (4) 3.4

80. 100 mL of ozone at STP was passed through 100 mL of '10 volume' H_2O_2 solution. What is the volume strength of H_2O_2 after reaction?
(1) 9.5 (2) 9.0
(3) 4.75 (4) 4.5

81. Select the correct statement.
(1) H_2O_2 can be stored in glass bottles
(2) Two (OH) groups in H_2O_2 lie in the same plane.
(3) Dilute solutions of H_2O_2 is concentrated by heating
(4) H_2O_2 is used to clean oil painting

82. Select the correct statement.
(1) Marshall acid is obtained when H_2O_2 reacts with one mole of $ClSO_3H$
(2) H_2O_2 with moist Ag_2O give silver peroxide
(3) Decomposition of H_2O_2 is accelerated by acetanilide.
(4) When BaO_2 or Na_2O_2 is reacted with dilute H_2SO_4, H_2O_2 is obtained

Multiple Correct Answers Type

Hydrogen and Hydrides

1. Which of the following is/are basic hydride?
(1) HCl (2) NH_3
(3) H_2S (4) PH_3

2. In which of the following property hydrogen does not resemble with halogen:
(1) atomicity (2) ionisation enthalpy
(3) reducing nature (4) electropositive nature

3. In the reaction of sodium hydride and water:
(1) Sodium is reduced
(2) Hydrogen is oxidised
(3) Hydrogen is reduced
(4) No element is oxidised or reduced

4. Which of the following elements are oxidised when they react with dihydrogen?
(1) Calcium (2) Sulphur
(3) Lithium (4) Carbon

5. What is true about saline hydrides?
(1) They are binary compounds of hydrogen and metallic elements.
(2) They are crystalline solids.
(3) They are generally very soft.
(4) Their common examples are, SiH_4, CH_4 etc.

6. Among the hydrides given below which are reasonably good acids?
(1) NH_3 (2) HF
(3) HN_3 (4) NaH

7. In which of the following hydrides, hydrogen exists in negative oxidation state?
(1) HCl (2) NaH
(3) CaH_2 (4) HI

8. Which of the following metals on treatment with NaOH will liberate H_2 gas?
(1) Zn (2) Sn
(3) Al (4) Mg

9. Select correct statements
(1) Para hydrogen has lower internal energy
(2) Ortho hydrogen has singlet state whereas para hydrogen has triplet state
(3) At absolute zero, hydrogen contains only Ortho form
(4) At the temperature of liquefaction of air, the ratio of Ortho and Para form of hydrogen is 1 : 1

10. Select incorrect statements
(1) Nascent hydrogen is more active than ordinary H_2
(2) Occluded hydrogen is less active and a stronger reducing agent than ordinary H_2
(3) Atomic hydrogen is more reactive than ordinary H_2, but less reactive than nascent and occluded (or adsorbed) hydrogen
(4) Pure Ortho hydrogen cannot be obtained.

Water

11. Which is false about ice?
(1) It has open cage-like structure.
(2) It has more density than water.
(3) Each O atom is surrounded by four H atoms.
(4) Each O atom has four H-bonds around it.

12. Permanent hardness is due to $Cl^{\ominus}$ and SO_4^{2-} of Mg^{2+} and Ca^{2+} and is removed by adding Na_2CO_3.
$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$
$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$
Which of the following statements is/are correct?
(1) If hardness is 100 ppm $CaCO_3$, the amount of Na_2CO_3 required to soften 10 L of hard water is 10.6 g.
(2) If hardness is 100 ppm $CaCO_3$, the amount of Na_2CO_3 required to soften 10 L of hard water is 10.6 g.
(3) If hardness is 420 ppm $MgCO_3$, the amount of Na_2CO_3 required to soften 10 L of hard water is 53.0 g.
(4) If hardness is 420 ppm $MgCO_3$, the amount of Na_2CO_3 required to soften 10 L of hard water is 5.3 g.

13. The hardness of water due to $HCO_3^{\ominus}$ is 122 pm.
Select the correct statement(s).
(1) The hardness of water in terms of $CaCO_3$ is 200 ppm.
(2) The hardness of water in terms of $CaCO_3$ is 100 ppm.
(3) The hardness of water in terms of $CaCO_3$ is 222 ppm.
(4) The hardness of water in terms of $CaCO_3$ is 95 ppm.

14. The reagent(s) used for softening the temporary hardness of water is (are):
(1) $Ca_3(PO_4)_2$ (2) $Ca(OH)_2$
(3) Na_2CO_3 (4) NaOCl

15. When zeolite, which is hydrated sodium aluminate silicate, is treated with hard water, the sodium ions are exchanged with:
(1) $Cl^{\ominus}$ (2) SO_4^{2-}
(3) Ca^{2+} (4) Mg^{2+}

16. Select the correct statement
(1) Degree of hardness in a water sample containing 111 ppm of $CaCl_2$ is 100 ppm
(2) Mg^{2+} and Ca^{2+} ions can be detected and estimated in hard water by titrating with disodium salt of EDTA using eriochrome black-T indicator
(3) Green vitriol contains 5 moles of H_2O coordinated with Fe^{2+} ion
(4) Sequestration is process of removing Ca^{2+} ions from hard water

Hydrogen Peroxide

17. Which of the following statements about the following reaction is/are not correct?
$Cr_2O_7^{2-} + 3H_2O_2 + 8H^{\oplus} \longrightarrow 2Cr^{3+} + 7H_2O + 3O_2$
(1) H_2O_2 is oxidised to O_2.
(2) H_2O is reduced to H_2O.
(3) The oxidation number of chromium atom changes by 3.
(4) Hydrogen ions are oxidised to H_2O.

18. Which of the following statements is/are correct about 6.8% strength of H_2O_2.
(1) Its normality is 4N.
(2) Its molarity is 2M.
(3) Its volume strength is 22.4V.
(4) Volume strength = 11.2 × M.

19. x g of H_2O_2 requires 100 mL of M/5 $KMnO_4$ in a titration in a solution having pOH = 1.0
Which of the following is/are correct?
(1) The value of x is 1.7 g.
(2) The value of x is 0.34 g.
(3) $MnO_4^{\ominus}$ changes to MnO_4^{2-}.
(4) H_2O_2 changes to O_2.

20. 20 mL of H_2O_2 is reacted completely with acidified $K_2Cr_2O_7$ solution. 40 mL of $K_2Cr_2O_7$ solution is required to oxidise the H_2O_2 completely. Also, 2.0 mL of the same $K_2Cr_2O_7$ solution is required to oxidise 5.0 mL of a 1.0M $H_2C_2O_4$ solution to reach equivalence point. Which of the following statements is/are correct?
(1) The H_2O_2 solution is 5M.
(2) The volume strength of H_2O_2 is 56V.
(3) The volume strength of H_2O_2 is 112V.
(4) If 40 mL more 5M/8H_2O_2 is further added to the 10 mL more H_2O_2 solution, the volume strength of the resulting solution is changed to 16.8 V.

21. The oxidation states of the most electronegative element in the products of the reaction between BaO_2 with dilute H_2SO_4 are
(1) –1 (2) +1
(3) –2 (4) 0

22. The oxides which give H_2O_2 on treatment with dilute acid are:
(1) PbO_2 (2) MnO_2
(3) Na_2O_2 (4) BaO_2

23. Which of the following equation shows the oxidizing nature of H_2O_2?
(1) $2[Fe(CN)_6]^{4-} + H_2O_2 + 2H^{\oplus} \longrightarrow 2[Fe(CN)_6]^{3-} + 2H_2O$
(2) $3N_2H_4 + 2H_2O \xrightarrow[\text{Catalyst}]{Cu^{2+}} N_2 + 4H_2O$
(3) $Hg + H_2O_2 \xrightarrow[H_2SO_4]{} HgO + H_2O$
(4) $AsO_3^{3-} + H_2O_2 \longrightarrow AsO_4^{3-} + H_2O$

24. Which of the following equation shows the reducing nature of H_2O_2?
(1) $H_2O_2 + NH_2OH \longrightarrow O_2 + NH_3 + H_2O$
(2) $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$
(3) $H_2O_2 + Pb_3O_4 + 6H^{\oplus} \longrightarrow 3Pb^{2+} + 4H_2O + O_2$
(4) $MnO_4^{\ominus} + 6H^{\oplus} + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

25. H_2O_2 can be prepared by the action of
(1) MnO_2 + dil. HCl $\longrightarrow$
(2) BaO_2 + Cold $H_3PO_4 \longrightarrow$
(3) BaO_2 +Cold $H_2SO_4 \longrightarrow$
(4) MgO_2 + Cold $H_2SO_4 \longrightarrow$

Linked Comprehension Type

Paragraph 1

H_2O_2 is reduced rapidly by Sn^{2+} to give H_2O and Sn^{4+}. H_2O_2 is decomposed slowly at room temperature to yield O_2 and H_2O.

136 g of 10% by mass of H_2O_2 in water is treated with 100 mL of 3 M Sn^{2+} and then a mixture is allowed to stand until no further reaction occurs.

The reactions involved are:

$2H^{\oplus} + H_2O_2 + Sn^{2+} \longrightarrow Sn^{4+} + 2H_2O$

$2H_2O_2 \longrightarrow 2H_2O + O_2$

1. The equivalent of H_2O_2 reacted with Sn^{2+} is
(1) 0.2 (2) 0.3
(3) 0.4 (4) 0.6

2. The equivalent of H_2O_2 left after reacting with Sn^{2+} is
(1) 0.1 (2) 0.2
(3) 0.3 (4) 0.4

3. The volume strength of H_2O_2 left after reacting with Sn^{2+} is
(1) 1.12 V (2) 11.2 V
(3) 2.24 V (4) 22.4 V

4. Calculate the volume of O_2 produced at 27°C and 1 atm after H_2O_2 is reacted with Sn^{2+} and the mixture is allowed to stand.
(1) 2.46 L (2) 4.92 L
(3) 1.23 L (4) 7.38 L

Paragraph 2

Hydrogen accounts for approximately 75% of the mass of the universe. Hydrogen serves as the nuclear fuel of our Sun and other stars, and these are mainly composed of hydrogen. On the earth, though hydrogen is rarely found in the uncombined state. Since the earth's gravity is too weak to hold such light molecules, nearly all the H_2 originally present in the earth's atmosphere has been lost to space. In the earth's crust and oceans, hydrogen is found in water, petroleum, proteins, carbohydrates and other compounds and it is the ninth most abundant element on a mass basis.

Hydrogen has three isotopes: hydrogen or protium ($_1^1H$), deuterium or heavy hydrogen (D or $_1^2H$), tritium (T or $_1^3H$).

The physical properties of the three isotopes are different due to the difference in their masses, i.e. isotope effect. The chemical properties of the three isotopes are similar as they have the same electronic configuration. Reaction between hydrogen and oxygen is highly exothermic, and gas mixtures that contain as little as 4% by volume hydrogen in oxygen (or in air) are highly flammable and potentially explosive.

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)} \qquad \Delta H = -484\ kJmol^{-1}$

As hydrogen is environmentally clean it is an enormously attractive fuel. 'Hydrogen economy' is an emerging field in which it is thought that our energy needs can be met by gaseous, liquid and solid hydrogen.

As hydrogen is not a naturally occurring substance such as coal, oil or natural gas, energy must be expanded to produce hydrogen before it can be used.

5. If an isotope of hydrogen has one neutron in its atom, its atomic number and atomic mass will respectively be:

(1) 1, 2 (2) 1, 3
(3) 1, 1 (4) 2, 1

6. Which of the following fuel produces least environmental pollution?

(1) Hydrogen (2) Coal
(3) Wood (4) Gasoline

7. Which of the following is radioactive in nature?

(1) Hydrogen only (2) Deuterium only
(3) Tritium only (4) Deuterium and tritium

8. Hydrogen, H_2, is very less abundant in the atmosphere due to

(1) inflammable nature of H_2
(2) weak earth's gravity which is not able to hold light H_2 molecules
(3) diatomic nature of hydrogen
(4) very rapid reaction between hydrogen and atmospheric oxygen

9. Liquid H_2 has been used as rocket fuel as

(1) its reaction with oxygen is highly exothermic
(2) it occupies small space
(3) it has high thrust
(4) all of the above

10. Which of the following is the lightest gas?

(1) Hydrogen (2) Oxygen
(3) Nitrogen (4) Helium

Paragraph 3

Hydrogen peroxide is a powerful oxidising agent, both in the acidic and alkaline medium.

In acidic medium: $H_2O_2 + 2H^{\oplus} + 2e^{\ominus} \longrightarrow 2H_2O$

In alkaline medium: $H_2O_2 + 2e^{\ominus} \longrightarrow 2\overset{\ominus}{O}H$

Hydrogen peroxide acts as a reducing agent towards powerful oxidising agents.

In acidic medium: $H_2O_2 \longrightarrow 2H^{\oplus} + O_2 + 2e^{\ominus}$

In alkaline medium, however, its reducing nature is more effective.

$H_2O_2 + 2\overset{\ominus}{O}H \longrightarrow 2H_2O + O_2 + 2e^{\ominus}$

11. On addition of H_2O_2 to acidified $KMnO_4$, $KMnO_4$ gets decolourised due to

(1) oxidation of $KMnO_4$
(2) reduction of $KMnO_4$
(3) both oxidation and reduction
(4) none of the above of $KMnO_4$

12. H_2O_2 behaves as a bleaching agent due to

(1) oxidising nature (2) reducing nature
(3) acidic nature (4) unstable nature

13. In the reaction, $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$, H_2O_2 behaves as

(1) an oxidising agent (2) a reducing agent
(3) acid (4) base

14. In which of the following reactions, H_2O_2 act as a reducing agent?

(1) $2KI + H_2O_2 \longrightarrow 2KOH + I_2$
(2) $KNO_2 + H_2O_2 \longrightarrow KNO_3 + H_2O$
(3) $Na_2SO_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O$
(4) $PbO_2 + H_2O_2 \longrightarrow PbO + H_2O + O_2$

15. In which of the following reactions, H_2O_2 acts as an oxidising agent?

(1) $2I^{\ominus} + H_2O_2 + 2H^{\oplus} \longrightarrow I_2 + 2H_2O$
(2) $IO_4^{\ominus} + H_2O_2 \longrightarrow IO_3^{\ominus} + H_2O + O_2$
(3) $Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$
(4) $2MnO_4^{\ominus} + 6H^{\oplus} + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

Paragraph 4

$$\text{Red hot coke} + \text{Steam} \xrightarrow{1000°C} \underset{\underset{\text{Steam}}{\uparrow}}{(X)} \xrightarrow[\text{Catalyst (Y)}]{500°C} (Z) + H_2$$

16. The above sequence refers to

(1) Lane's process (2) Bosch's process
(3) Ostwald's process (4) Haber's process

17. 'X' is

(1) water gas (2) producer gas
(3) coal gas (4) oil gas

18. 'Z' is

(1) CO (2) CO_2
(3) O_2 (4) H_2O

19. Catalyst 'Y' is

(1) V_2O_5 (2) Cr_2O_3
(3) Fe_2O_3 (4) $Fe_2O_3 + Cr_2O_3$

20. 'Z' is removed by passing the gaseous mixture through

(1) acidic solution
(2) alkaline solution
(3) water under high pressure of 25 atm
(4) an organic solvent

Matrix Match Type

This section contains questions each with two columns I and II. Match the items given in column I with that in the column II.

1.

	Column I		Column II
a.	Calgon	**i.**	More reactive form of hydrogen as compared to H_2
b.	D_2O	**ii.**	Open book-type structure
c.	Nascent hydrogen	**iii.**	Sodium polymeta-phosphate
d.	H_2O_2	**iv.**	Heavy water

2.

	Column I		Column II
a.	Fe_3O_4	i.	Metallic hydride
b.	Non-stoichiometric compound	ii.	Mixed oxide, formed as one product in Lane's process
c.	Covalent hydride	iii.	Hydrolith
d.	Salt-like hydride	iv.	Hydrogen compounds of non-metals

3.

	Column I		Column II
a.	$NaBH_4$	i.	Complex hydride
b.	$LiBH_4$	ii.	Alanate
c.	BeH_2	iii.	Ionic hydride
d.	LiH	iv.	Covalent hydride

4.

	Column I		Column II
a.	Sodium ion in zeolite gets exchanged with	i.	Ca^{2+}
b.	Hardness	ii.	Mg^{2+}
c.	Temporary hardness	iii.	$Ca(HCO_3)_2$
d.	Permanent hardness	iv.	$MgSO_4$

5. Match the items given in Column I with that in Column II and III.

	Column I		Column II		Column III
a.	Ortho-hydrogen	i.	Spins of the nuclei in opposite direction	p.	Less stable. 50% more thermal conductivity
b.	Para-hydrogen	ii.	Atomic hydrogen	q.	Reduction of $FeCl_3$ (yellow) to $FeCl_2$ (faint green)
c.	$Zn + 2NaOH \rightarrow Na_2ZnO_2 +$	iii.	Spins of the nuclei in the same direction	r.	More reactive than various forms of hydrogen
d.	H_2 is heated with tungten or platinum wire by an electric current it gives	iv.	Nascent hydrogen	s.	More stable. Less thermal conductivity

6. Match the items given in Column I with that in Column II and III.

	Column I		Column II		Column III
a.	Hydride gap elements	i.	Non-stoichio-metric hydrides	p.	Do not form hydride
b.	Metallic hydride or interstitial hydrides	ii.	Group 15 to 17	q.	Exist in polyymeric forms
c.	Electron-deficient molecular hydrides	iii.	Group 7 to 9	r.	$ZrH_{1.3\text{-}1.75}$ $VH_{0.56}$
d.	Electron-rich molecular hydrides	iv.	B_2H_6, B_4H_{10}	s.	Exist as associated molecules due to intermolecular H-bonds

Numerical Value Type

1. What is the molarity of H_2O_2 of the 11.2 V (volume strength)?
2. A bottle of H_2O_2 is labelled as 10 vol H_2O_2. 112 mL of this solution of H_2O_2 is titrated against 0.04 M acidified solution of $KMnO_4$. Calculate the volume of $KMnO_4$ in terms of litre.
3. What is the oxidation state of oxygen of H_2O_2 in the final products when it reacts with $ClO_3^{\ominus}$?
4. What is the oxidation state of oxygen of H_2O_2 in the final products when it reacts with As_2O_3?
5. Washing soda ($Na_2CO_3 \cdot 10H_2O$) is widely used in softening of hard water. If 1 L of hard water requires 0.0143g of washing soda, what is hardness of water in terms of ppm of $CaCO_3$?
6. What is the sum of protons, electrons and neutrons in the heaviest isotope of hydrogen?
7. What is the sum of protons, electrons and neutrons in the lightest isotope of hydrogen?
8. How many moles of ammonia are produced when one mole of calcium nitride reacts with water?
9. How many moles of phosphine are produced when one of the calcium phosphides reacts with water?
10. What is the molarity of a commercial sample of 33.6 volume hydrogen peroxide solution?

Archives

JEE MAIN

Single Correct Answer Type

1. *Ortho* and *para* hydrogen have
   (1) identical chemical properties but different physical properties
   (2) identical physical and chemical properties
   (3) identical physical properties but different chemical properties
   (4) different physical and chemical properties
   (AIEEE 2009)

2. $$CO + H_2 \xrightarrow[\text{X (Catalyst)}]{300^\circ/300\text{ atm}} CH_3OH$$
   The catalyst 'X' is
   (1) Fe (2) Cr_2O_3/ZnO
   (3) V_2O_5 (4) Al_2O_3 **(AIEEE 2009)**

3. Which of the following undergoes reduction with H_2O_2 in an alkaline medium?
   (1) Mn^{2+} (2) HOCl
   (3) PbS (4) Fe^{2+} **(AIEEE 2010)**

4. In the reaction,
   $$H_2S + H_2O_2 \longrightarrow S + 2H_2O$$
   (1) H_2S is an acid and H_2O_2 is a base
   (2) H_2S is a base and H_2O_2 is an acid
   (3) H_2S is an oxidizing agent and H_2O_2 is a reducing agent
   (4) H_2S is a reducing agent and H_2O_2 is an oxidizing agent
   (AIEEE 2010)

5. Very pure hydrogen (99.9%) can be made by which of the following processes?
   (1) Mixing natural hydrocarbons of high molecular weight
   (2) Electrolysis of water
   (3) Reaction of salt like hydrides with water
   (4) Reaction of methane with steam **(AIEEE 2012)**

6. In the reaction,
   $$2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O$$
   The oxidizing agent is:
   (1) $FeSO_4$ (2) H_2SO_4
   (3) H_2O_2 (4) both H_2SO_4 and H_2O_2
   (JEE Main 2013)

7. The molecular formula of a commercial resin used for exchanging ions in water softening is $C_8H_7SO_3Na$ (Mol. wt. 206). What would be the maximum uptake of Ca^{2+} ions by the resin when expressed in mole per gram resin?
   (1) $\frac{1}{103}$ (2) $\frac{1}{206}$
   (3) $\frac{2}{309}$ (4) $\frac{1}{412}$ **(JEE Main 2015)**

8. From the following statements regarding H_2O_2, choose the incorrect statement:
   (1) It can act only as an oxidizing agent
   (2) It decomposed on exposure to light
   (3) It has to be stored in plastic or wax lined glass bottles in dark
   (4) It has to be kept away from dust **(JEE Main 2015)**

9. Hydrogen peroxide oxidises $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ in acidic medium but reduces $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ in alkaline medium. The other products formed are, respectively:
   (1) $(H_2O + O_2)$ and $(H_2O + OH^-)$
   (2) H_2O and $(H_2O + O_2)$
   (3) H_2O and $(H_2O + OH^-)$
   (4) $(H_2O + O_2)$ and H_2O **(JEE Main 2018)**

JEE ADVANCED

Single Correct Answer Type

1. The reagent used for softening the temporary hardness of water is/are
   (1) $Ca_3(PO_4)_2$ (2) $Ca(OH)_2$
   (3) Na_2CO_3 (4) NaOCl
   (IIT-JEE 2010)

Multiple Correct Answers Type

1. The reagent (s) used for softening the temporary hardness of water is(are).
   (1) $Ca_3(PO_4)_2$ (2) $Ca(OH)_2$
   (3) Na_2CO_3 (4) NaOCl
   (IIT-JEE 2010)

2. Hydrogen peroxide in its reaction with KIO_4 and NH_2OH respectively, is acting as a
   (1) reducing agent, oxidising agent
   (2) reducing agent, reducing agent
   (3) oxidising agent, oxidising agent
   (4) oxidising agent, reducing agent
   (JEE Advanced 2014)

Answers Key

ERCISES

ngle Correct Answer Type

1. (4) 2. (1) 3. (3) 4. (1) 5. (3)
6. (1) 7. (4) 8. (4) 9. (2) 10. (3)
11. (2) 12. (4) 13. (3) 14. (2) 15. (3)
16. (4) 17. (4) 18. (2) 19. (1) 20. (1)
21. (1) 22. (1) 23. (4) 24. (4) 25. (1)
26. (2) 27. (1) 28. (3) 29. (1) 30. (2)
31. (1) 32. (3) 33. (2) 34. (2) 35. (3)
36. (4) 37. (1) 38. (3) 39. (3) 40. (2)
41. (1) 42. (2) 43. (4) 44. (4) 45. (3)
46. (2) 47. (2) 48. (2) 49. (4) 50. (4)
51. (2) 52. (3) 53. (3) 54. (4) 55. (1)
56. (2) 57. (4) 58. (2) 59. (2) 60. (1)
61. (4) 62. (1) 63. (1) 64. (4) 65. (2)
66. (1) 67. (2) 68. (4) 69. (3) 70. (4)
71. (2) 72. (2) 73. (1) 74. (1) 75. (3)
76. (2) 77. (2) 78. (1) 79. (4) 80. (1)
81. (4) 82. (4)

Multiple Correct Answers Type

1. (2, 4) 2. (3, 4) 3. (2, 3)
4. (1, 3) 5. (1, 4) 6. (2, 3)
7. (2, 3) 8. (1, 2, 3) 9. (1, 4)
10. (2, 3) 11. (2, 4) 12. (1, 4)
13. (2, 4) 14. (2, 3) 15. (3, 4)
16. (1, 2, 4) 17. (2, 4) 18. (1, 2, 3, 4)
19. (2, 3, 4) 20. (1, 2, 4) 21. (1, 3)
22. (3, 4) 23. (1, 2, 3, 4) 24. (1, 2, 3, 4)
25. (2, 3)

Linked Comprehension Type

1. (4) 2. (2) 3. (2) 4. (3) 5. (1)
6. (2) 7. (3) 8. (2) 9. (4) 10. (1)
11. (2) 12. (1) 13. (2) 14. (4) 15. (1)
16. (2) 17. (1) 18. (2) 19. (4) 20. (3)

Matrix Match Type

Q. No.	a	b	c	d
1.	iii	iv	i	ii
2.	ii	i	iv	iii
3.	i	i, ii	iv	iii
4.	i, ii	i, ii	iii	iv
5.	iii, s	i, p	iv, q	ii, r
6.	iii, p	i, r	iv, q	ii, s

Numerical Value Type

1. (1) 2. (1) 3. (0) 4. (2) 5. (5)
6. (4) 7. (2) 8. (2) 9. (2) 10. (3)

ARCHIVES

JEE Main

Single Correct Answer Type

1. (1) 2. (2) 3. (2) 4. (4) 5. (2)
6. (3) 7. (4) 8. (1) 9. (2)

JEE Advanced

Single Correct Answer Type

1. (2)

Multiple Correct Answers Type

1. (2, 3, 4) 2. (1)

4 s-Block Group 1 Elements Alkali Metals

OVERVIEW

Group 1: Alkali Metals

1. General electronic configuration: ns^1.
2. Highly reactive and hence do not occur in the free state but widely distributed in nature in the combined form as halides, oxides, silicates, borates and nitrates.
3. They are called alkali metals because they dissolve in water and produce hydroxides which are basic or alkaline in nature. They have metallic properties.
4. They have similar chemical properties but they do not occur together due to the different sizes of their ions.
5. Na is 7th, K is the 8th and Li is the 35th most abundant element by weight in the earth's crust.
6. Na and Mg are also present in relatively large amounts in sea water, brine wells and a few salt lakes.
7. K and Ca also occur to smaller extent in sea water.
8. Na and K are almost equally abundant (2.83% Na and 2.59% K) in the earth's crust, but sea water contains 2.8% NaCl and only 0.8% KCl.

   It is due to that much of K that appears in ground water from dissolved minerals is taken up preferentially by plants while $Na^{\oplus}$ ion goes to the sea water.
9. The remaining elements are much less abundant, i.e. Rb is the 23rd, Cs is the 46th most abundant element by weight in the earth's crust, while Fr is extremely rare and is radioactive. Fr was discovered by Pierre (1939), at the Curie Institute, Paris. Isotope of Fr, i.e. Fr^{233} have the longest half life of 21 minutes.
10. Li mainly occurs in the form of silicates, i.e. spodumene $[LiAl(SiO_3)_2]$ and lepidolite $[(Li, Na, K)_2Al_2(SiO_3)_3F(OH)_2]$ and amblygonite $[LiAl(PO_4)F]$.
11. Important minerals of Na are rock salt (NaCl), borax $(Na_2B_4O_7 \cdot 10H_2O)$, trona $(Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O)$, chile salt petre $(NaNO_3)$ and mirabilite (Na_2SO_4).
12. K mainly occurs as sylvite/sylvine (KCl), carnalite $(KCl \cdot MgCl_2 \cdot 6H_2O)$ and feldspar $(K_2O \cdot Al_2O_3 \cdot 6SiO_2)$.
13. The following properties decrease down the group (↓):
    a. IE_1, IE_2, EN, melting and boiling points
    b. Hydration enthalpy and lattice enthalpy
    c. Charge density and polarising power
    d. Reactivity towards hydrogen
14. The following properties increase down the group (↓):
    a. Atomic number and atomic mass
    b. Metallic radius and ionic radius $(M^{\oplus})$
    c. Density (g cm^{-3}) (exception, density of K < density of Na)
    d. Reactivity towards water and oxygen
15. **Flame colouration:**

Metal	Li	Na	K	Rb	Cs
Colour	Crimson	Yellow	Pale violet	Red violet	Blue

    Heat from the flame excites the outermost orbital electron to a higher energy level. When these e^-'s return to the ground state, there is emission of radiation in the visible region.
16. Li is the strongest reducing agent in aqueous solution. Since Li has the most negative standard reduction potential ($E^{\ominus} = -3.04$ V). Moreover, the high IE_1 of lithium is more than compensated by the high (negative) hydration enthalpy. The decreasing order of reducing character in aqueous solution is Li > Cs > Rb > K > Na.
17. **Reactivity towards oxygen increases down the group (↓):** Li forms monoxide (Li_2O), Na forms peroxide (Na_2O_2), while K, Rb and Cs form superoxides (MO_2, where M = K, Rb and Cs) at similar condition.

    This is due to the fact that comparable sizes of the ions form the strongest lattice.
18. **Solubility in liquid ammonia:** They dissolve in liquid ammonia (up to 5 M) giving highly conducting deep blue solution, due to the formation of ammoniated electrons. The solution contains also ammoniated cations. Up to 3M concentration of NH_3, the solution is dark blue in colour and when the concentration of NH_3 is greater than 3M, the colour changes to copper-bronze and the solution acquires metallic lusture due to the formation of metal ion cluster.

    The blue-coloured solutions are paramagnetic due to the presence of large number of unpaired electrons but bronze solutions are diamagnetic due to the formation of electron clusters in which ammoniated electrons with opposite spin group together, i.e.

    $2e^{\ominus}(NH_3)_y \rightarrow [\uparrow e^{\ominus}(NH_3)_y[\downarrow e^{\ominus}(NH_3)_y]$

The solution of alkali metals in liquid NH_3 has proved to be a good conductor of electricity due to the presence of ammoniated electrons and ammoniated cations.

But the conductivity decreases as the concentration of NH_3 increases. This is due to the fact that the ammoniated metal cations are bounded by the free unpaired electrons and this situation is referred to as *expanded metals*.

19. Basic strength of hydroxides of alkali metals: Basic strength of alkali metals increase down the group (↓) due to their low IE's.

All hydroxides of alkali metals are highly soluble in water and thermally stable except LiOH which decomposes on heating to give Li_2O.

$$2LiOH \xrightarrow{\Delta} Li_2O + H_2O$$

20. Reactivity towards halogens

Li Na K Rb Cs ↓	Reactivity of alkali metals with particular halogens increases	F_2 Cl_2 Br_2 I_2 ↓	Reactivity of halogens with particular alkali metal decreases

For any given alkali metals, the reactivity decreases in the order:

Fluoride > Chloride > Bromide > Iodide

Thus, fluorides are the most stable while iodides are least stable, because $\Delta_f H^{\ominus}$ values for fluorides become less and less negative down the group (↓). Whereas for chlorides, bromides and iodides, $\Delta_f H^{\ominus}$ value becomes more and more negative down the group (↓).

21. Lattice enthalpies ($\Delta_U H^{\ominus}$) and hydration enthalpies ($\Delta_{Hyd} H^{\ominus}$): Both lattice and hydration enthalpies decrease down the group (↓).

a. Greater (more negative) the lattice enthalpy, higher is the melting point of the alkali metal halides and lower is its solubility in water.

b. Greater (more negative) the hydration enthalpy (i.e. sum of the hydration enthalpies of cations and anions), greater is the solubility of the compound in water.

c. The ionic mobilities of alkali metal ions in aqueous solution should be: $Li^{\oplus} > Na^{\oplus} > K^{\oplus} > Rb^{\oplus} > Cs^{\oplus}$ due to the decreasing order of charge densities (ionic charge/ionic size). But the observed order is reverse of the above, i.e. $Li^{\oplus} < Na^{\oplus} < K^{\oplus} < Rb^{\oplus} < Cs^{\oplus}$, due to the decreasing order of extent of hydration.

d. Similarly, the order of hydrated radius (in pm) of alkali metal ions is $Li^{\oplus}(340) > Na^{\oplus}\ (276) > K^{\oplus}\ (232) > Rb^{\oplus}\ (228) > Cs^{\oplus}\ (226)$.

e. Solubility of LiF in H_2O is low due to its high lattice enthalpy whereas the low solubility of CsI is due to less (negative) value of the hydration enthalpies of two ions (-670 kJ mol^{-1}).

f. The solubility of most of alkali metal halides (except those of fluorides) decreases down the group (↓). It is due to the fact that decrease in hydration enthalpy is more than the corresponding decrease in its lattice enthalpy.

g. Thus NaCl is more soluble in H_2O than KCl, because the difference in lattice enthalpy between NaCl and KCl is 68 kJ mol^{-1} but the difference in hydration enthalpy of $Na^{\oplus}$ and $K^{\oplus}$ ions is 75 kJ mol^{-1}.

h. The solubility of alkali metal fluorides increases from LiF to CsF, because the decrease in lattice enthalpy is more than compensates the decrease in hydration enthalpy.

22. Ionic and covalent character of alkali metal halides (polarisation effect): According to Fajans' rule, polarising power (covalent character) ∝ smaller cation ∝ larger anion ∝ greater charge on cation or anions ∝ pseudo noble gas configuration, i.e. having 18 e^-'s in the outermost shell. For example:

a. The covalent character decreases as the size of the cation increases, i.e. LiCl > NaCl > KCl > RbCl > CsCl. Thus, LiCl is more covalent than KCl.

b. The covalent character decreases as the size of anion decreases, i.e. LiI > LiBr > LiCl > LiF. That is why the dipole moment (μ) of LiF (11.6D) is greater than the dipole moment (μ) of LiI (6.26D).

c. The covalent character of some of the halides decreases in the order as the charge on the cation decreases (charge on anion is constant),

$$\overset{+3}{Al}\,\overset{-1\times3}{Br_3} > \overset{+2}{Mg}\,\overset{-1\times2}{Br_2} > \overset{+1}{Na}\,\overset{-1}{Br}$$

d. The covalent character of some of the compounds of alkali metal decreases in the order as the charge on the anion decreases (charge on cation is constant).

$$\overset{+1\times3}{K_3}\,\overset{-3}{PO_4} > \overset{+1\times2}{K_2}\,\overset{-2}{SO_4} > \overset{+1}{K}\,\overset{-1}{Cl}$$

e. CuBr is more covalent than NaBr, although $Cu^{\oplus}$ and $Na^{\oplus}$ have the same charge +1, and nearly the same size, i.e. $Cu^{\oplus}$ (0.96 Å) and $Na^{\oplus}$(1.02 Å). This is due to the fact that $Cu^{\oplus}$ ion has a pseudo noble gas configuration, i.e. having 18 e^-'s in the outermost shell.

23. Melting point:

a. For the same alkali metal, the melting points decrease in the order:

Fluoride > chloride > bromide > iodide

This is due to the decrease in lattice enthalpies as the size of the halide ion increases (size of cation is constant), e.g.

NaF(1261K) > NaCl(1084K) > NaBr > NaBr(1028K) > NaI(944K)

b. For the same halide ion, the melting points decrease down the group (↓), i.e. from Na to Cs, due to the decrease in lattice enthalpies as size of cation increases.

NaCl (1085 K) > KCl (1040 K) > RbCl (1000 K) > CsCl (928K)

Note: The melting point of lithium halides is lower than other alkali metal halides.

The melting point of LiCl (887 K) is lower than NaCl (1084 K), because LiCl is covalent and NaCl is ionic in character (small size of cation, i.e. size of $Li^{\oplus}$ < size of $Na^{\oplus}$).

24. **Salts of oxoacids**: Alkali metal hydroxides are strong bases and hence they form salt with all oxoacids (HNO_3, HNO_2, H_2SO_4, H_2CO_3, H_3PO_4). They are generally soluble in H_2O and stable towards heat.

25. a. **Carbonates and bicarbonates**: All of them are soluble in H_2O and their solubilities increase down the group (↓) because lattice enthalpies decrease more rapidly than their hydration enthalpies down the group (↓).

b. The carbonates of alkali metals (M_2CO_3) are stable up to 1275 K, above which they decompose to form oxides.

c. Li_2CO_3 is less stable and decomposes readily to give ($Li_2O + CO_2$).

d. No other metals form solid bicarbonates except alkali metals, though NH_4HCO_3 also exists as a solid.

Exception: Lithium does not form solid bicarbonates but exists in solution.

e. All the alkali metal bicarbonates on heating decomposes to give carbonates, CO_2 and H_2O.

$$2MHCO_3 \xrightarrow{\Delta} M_2CO_3 + CO_2 + H_2O$$

26. **Anomalous behaviour of lithium**: Due to its small size, high charge density (charge/size ratio), high IE, non-availability of *d*-orbitals in its valence shell, and strong intermetallic bonding, some of the properties of Li differ from the other members of its group, e.g.

a. It forms nitrides with N_2.

b. LiOH and Li_2CO_3 decompose on heating to give Li_2O.

c. $LiNO_3$ decomposes on heating to give $Li_2O + NO_2 + O_2$, while others give $MnO_2 + O_2$.

d. LiCl is deliquescent and forms hydrate ($LiCl{\cdot}2H_2O$), while others do not form hydrates.

e. LiOH is a weaker base than others.

f. Halides of Li (e.g. LiCl) are covalent.

g. Li does not react with acetylene while others react to form metal acetylide. But Li, on heating with C, forms lithium acetylide while others do not react with C directly.

h. $LiHCO_3$ does not form a solid.

i. $Li^{\oplus}$ ion is the largest hydrated ion.

j. Li is harder and have higher melting and boiling points.

k. Li forms Li_2O, while Na forms Na_2O_2 and others form superoxides (KO_2) with O_2.

27. **Diagonal relationship of Li with Mg**: Due to the similarity in charge densities (charge/size ratio) of Li and Mg, they resemble in some of their properties, e.g.

a. Both form nitrides with N_2 (Li_3N and Mg_3N_2).

b. Hydroxides of both decompose on heating to Li_2O and MgO, respectively.

c. Compounds of both are deliquescent and form hydrates ($LiCl_2{\cdot}H_2O$ and $MgCl_2{\cdot}6H_2O$).

d. Both do not form solid bicarbonates.

e. Both form oxides with O_2 (Li_2O and MgO, respectively).

f. Nitrates of both decompose on heating to give their oxides (Li_2O and MgO, respectively) and $NO_2 + O_2$.

g. The hydroxides, carbonates and fluorides of both are sparingly soluble in H_2O.

28. **Extraction of alkali metals:**

a. They are strong reducing agents and hence cannot be extracted by reduction of their oxides and chlorides.

b. They cannot be obtained by the electrolysis of aqueous solutions of their salts since $E^{\ominus}$ red of H_2O is greater than $E^{\ominus}$ red of alkali metals. So, $H_{2(g)}$ is obtained at cathode.

c. They cannot be displaced from the aqueous solution of their salts by other metals due to their high electropositive character.

d. That is why they are obtained by the electrolysis of their molten (fused) salts usually chlorides.

e. Melting points of their chlorides are very high, so some suitable salts (e.g. CaF_2, KF etc.) are added to lower down the melting points of their chlorides.

29. **Extraction of Li:** It is obtained by electrolysis of a fused mixture of dry LiCl (55%) and KCl (45%). It cannot be stored in kerosene oil since it floats on the surface because of its very low density. It is the lightest metal known (density = 0.53 g cm^{-3}).

Uses:

a. In the preparation of alloys:

i. White metal (or Li–Pb) alloy (0.05% Li)

ii. Li–Al alloys

iii. Li–Mg alloys (14% Li)

b. To make electrochemical cells.

30. **Extraction of Na and its uses:** It is obtained by the electrolysis of fused mixture of NaCl (40%) + $CaCl_2$(60%) in a Down's cell at 873 K using graphite anode and iron cathode.

Uses:

a. It is used to make tetraethyl lead $Pb(C_2H_5)_4$, which is used as *anti-knocking agent for gasoline.*

b. Used in sodium vapour lamps.

c. Used as a reducing agent in the extraction of B and Si.

d. Used as a reagent in Wurtz reaction and in the synthesis of many organic compounds.

31. **Extraction of K and its uses:** It cannot be obtained by the electrolysis of fused KCl because K metal is more soluble in KCl, therefore it is obtained by the electrolysis of fused KOH, K is obtained at cathode and O_2 at anode. It can also

be obtained by the reduction of KCl with Na vapours at about 1130 K in a large fractionating column.

Uses: K plays a very vital role in biological system.

32. a. Compounds of Na:

i. Sodium carbonate (washing soda) $Na_2CO_3 \cdot 10H_2O$. It is prepared by **Solvay-ammonia process.**

Raw matcrals used: Brine (NaCl) solution saturated with NH_3 and $CaCO_3$ (for the production of CO_2).

It is used for softening of hard water.

ii. K_2CO_3 cannot be prepared by the **Solvay process.** $NaHCO_3$ is sparingly soluble in H_2O, while $KHCO_3$ is fairly soluble in H_2O. So, $NaHCO_3$ is precipitated whereas $KHCO_3$ does not precipitate when CO_2 is passed through an ammonical solution of KCl.

b. Sodium chloride (common salt or table salt) NaCl: It is produced by solar evaporation of sea water. Crude NaCl obtained by crystallisation of brine solution contains impurities of Na_2SO_4, $CaSO_4$, $CaCl_2$ and $MgCl_2$.

The pure NaCl is obtained by passing HCl gas through the aqueous solution of crude NaCl. It is used in the preparation of Na_2CO_3, Na_2O_2 and NaOH.

c. Caustic soda (NaOH): It is prepared by the electrolysis of an aqueous solution of NaCl using mercury cathode and graphite anode in a vessel called **Castner and Kellner's cell or mercury cathode cell.**

d. Baking soda (sodium hydrogen carbonate) $NaHCO_3$: It is prepared by saturating a solution of Na_2CO_3 with CO_2. Due to its less solubility in H_2O, white crystals of $NaHCO_3$ are precipitated.

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

It is used in the preparation of *baking powder*, which is a mixture of $NaHCO_3$(30%), starch (40%), $Ca(H_2PO_4)_2$ (calcium dihydrogen phosphate) (10%) and $NaAl(SO_4)_2$ (sodium aluminium sulphate) (20%). It is used as an antacid.

33. Biological importance of Na and K: $Na^{\oplus}$ ions are found outside the cell in blood plasma and other interstitial fluids, $K^{\oplus}$ ions are present inside the cell. These ions help in regulating the flow of water across the cell membrane, in transmission of nerve signals, and in the transport of sugars and amino acids into the cell.

$K^{\oplus}$ ions activate many enzymes and participate in the oxidation of glucose to ATP. Due to different concentration of $Na^{\oplus}$ and $K^{\oplus}$ ions on the opposite sides of cell membrane so Na–K pump operates across the cell which consumes more than one-third of the ATP used by a resting human being.

34. Some important information:

a. Li is not used in photoelectric cell because of highest IE among alkali metals.

b. The compounds of the first and second groups are colourless (unless anion is coloured like $MnO_4^{\ominus}$ and $Cr_2O_7^{2-}$, due to the charge transfer theory) and diamagnetic, because their ions $M^{\oplus}$ and M^{2+} have noble gas configuration with no unpaired electrons.

c. Peroxides (O_2^{2-}) of the first group are colourless and diamagnetic while superoxides ($O_2^{\ominus}$) are coloured and paramagnetic.

d. i. The first group metals can be induced to form normal oxides, i.e. monoxides (O^{2-}), peroxides (O_2^{2-}) and superoxides ($O_2^{\ominus}$) by dissolving metals in liquid NH_3 and passing appropriate amount of O_2.

ii. Except Cs_2O, all other monoxides, e.g. Li_2O, Na_2O, K_2O and Rb_2O have antifluorite structures. Cs_2O has anti $CdCl_2$ layer structure.

iii. Potassium superoxide (KO_2) combines directly with CO_2 forming K_2CO_3 and with CO_2 and the moisture forming $KHCO_3$, e.g.

$$4KO_2 + 2CO_2 \longrightarrow 2K_2CO_3 + 3O_2$$

$$4KO_2 + 4CO_2 + 2H_2O \longrightarrow 4KHCO_3 + 3O_2$$

e. Both KO_2 and Na_2O_2 are used as a source of oxygen (or for the purification of air) in confined space such as submarines, space shuttles and in emergency breathing instrument such as oxygen masks. The moisture of the breath reacts with KO_2 or Na_2O_2 to liberate O_2 and simultaneously KOH and NaOH formed remove CO_2 as it is exhaled, thereby allowing the atmosphere in the mask to be continuously regenerated.

$$4KO_{2(s)} + 2H_2O_{(g)} \rightarrow 4KOH_{(aq)} + 3O_{2(g)}$$

$$2Na_2O_{2(s)} + 2H_2O_{(g)} \rightarrow 4NaOH_{(aq)} + O_{2(g)}$$

$$KOH_{(aq)} \text{ or } NaOH_{(aq)} + CO_{2(g)} \rightarrow KHCO_{3(s)} \text{ or } NaHCO_{3(s)}$$

f. LiOH is also used to remove CO_2 from exhaled air in confined space such as submarines and space shuttles.

g. Potassium ozonide (KO_3) is an orange-coloured solid and contains paramagnetic $O_3^{\ominus}$ ion and is prepared by passing O_3 through KOH solution.

h. All metals of the first group exist as *bcc* structure with a coordination number of 8.

i. Li does not form alums due to its very small size.

j. Group 1 metals combine with Hg to form amalgams with the release of energy.

k. Alkali metals react with halogens and interhalogens to form ionic polyhalide compounds, e.g.

$$NaI + I_2 \rightarrow NaI_3$$

$$NaBr + ICl \rightarrow Na[Br\ ICl]$$

$$NaF + BrF_3 \rightarrow Na[BrF_4]$$

l. Lithia water is an aqueous solution of $LiHCO_3$ and is used for the treatment of gout.

4.1 INTRODUCTION

The elements as arranged in the modern periodic table have been divided into four blocks, namely *s*-, *p*-, *d*- and *f*-block. This classification has been done on the basis of the nature of the sub-shell into which the differentiating electron, i.e. the last electron enters. The elements in which the last electron enters the *s*-orbital are called *s-block elements*. As *s*-orbital can accommodate only two electrons, hence it has two groups:

1. Group 1 elements or alkali metals and
2. Group 2 elements or alkaline earth metals

The general electronic configuration of *s*-block elements is ns^{1-2}.

Group 1 consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the *alkali metals* after the Arabic word *al-qis* meaning plant ashes because ashes of plants are particularly rich in the carbonates of sodium and potassium. The elements of group 2 include beryllium, magnesium, calcium, strontium, barium and radium. These elements with the exception of beryllium are commonly known as the *alkaline earth metals*.

A regular trend is observed in the physical and chemical properties of group 1 elements with increasing atomic number. The loosely held *ns*-electrons in these elements make them the most electropositive elements, forming $M^{\oplus}$ ion. The same relationship is observed in group 2 elements also. Group 2 elements with two electrons in the valence shell are highly electropositive and form M^{2+} ions.

4.1.1 ANOMALOUS BEHAVIOUR OF HEAD ELEMENTS

The elements belonging to the second period (lithium, beryllium etc.) are sometimes called *head elements* of their respective groups. The first element in groups 1, 2, 13, 14, 15, 16 and 17 exhibits certain properties which are different from that of other elements in respective groups. This anomalous behaviour of the first element in each group can be attributed to:

- Small size of the atoms and ions.
- High ionisation energy and electronegativity.
- High polarising power of ions.
- Absence of *d*-orbitals in the valence shells.

4.1.2 DIAGONAL RELATIONSHIP

In addition to the group and period relationships, the elements of *s*- and *p*-block elements also exhibit a diagonal relationship. On moving diagonally across the periodic table, the elements show certain similarities which are however far less pronounced than the similarities within a group. The diagonal relationship is particularly noticeable in the elements of the second and third periods of the periodic table. The most important diagonal pairs are lithium and magnesium, beryllium and aluminium, and boron and silicon.

	Group 1	Group 2	Group 13	Group 14
Period 2	Li ↘	Be ↘	B ↘	C
Period 3	Na	Mg	Al	Si

Main reasons for the diagonal relationship:

1. Along the period (→), the size of the element decreases, whereas down the group (↓), the size of the element increases. The size of diagonally placed elements of the second and third periods will therefore be similar.
2. Along the period (→), the electronegativity and ionisation energy increases, whereas down the group (↓), both these properties decrease. Hence, diagonally placed elements will have identical electronegativity and ionisation energy.
3. Along the period (→), the charge density (charge/radius ratio) and polarising power [ionic charge/(ionic radius)^2 ratio] increase due to the decrease in size and the increase in charge. However, down the group (↓), the charge density and polarising power decrease due to the increase in size. On moving diagonally, these two effects almost balance each other, resulting in similar charge density and polarising power of the elements.

   All the physical and chemical properties of the elements depend upon the above three factors. Hence, the diagonally placed elements exhibit similarity in their properties.

   a. Similarity in the properties of Li and Mg is mainly due to similar charge density.
   b. Similarity in the properties of Be and Al is due to the same charge density and electronegativity.
   c. Similarity in the properties of B and Si is due to similar size, ionisation energy and electronegativity.

4.2 GROUP 1 ELEMENTS: ALKALI METALS

Group 1 consists of lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr). Group 1 elements are also known as alkali metals, since all the elements are metallic in character and their oxides react with water to give hydroxides which are strong alkalis or bases.

Origin of the name:

1. The name *lithium* is derived from the Greek word 'lithos' which means stone.
2. The name *sodium* is derived from the word 'soda', which itself is derived from an Arabic word meaning 'to split apart', since it was first used as a remedy for splitting headache.
3. The name *potassium* is derived from the word 'potash' which means 'ash of plants' because they are rich in potassium carbonate (K_2CO_3).
4. The name *rubidium* is derived from the Latin word 'rubidus' which means bright red. Rubidium was given this name after two bright red lines were observed in its spectra.
5. The name *caesium* is derived from the Latin word 'caesius' which means bluish grey. It was given this name when blue lines were observed in its spectra.
6. *Francium* was discovered in 1939 by M. Perey at Curie Institute, Paris. At her suggestion, the element was named as 'Francium', after her native land France.

4.3 ABUNDANCE AND OCCURRENCE

Among the alkali metals, sodium and potassium are abundant; lithium, rubidium and caesium have much low ratios of abundance. Francium is radioactive [all the elements heavier than bismuth (atomic number 83) are radioactive] and is formed in the natural radioactive decay and in nuclear reactions. All its isotopes are radioactive; the longest lived isotope $^{223}_{87}Fr$ has a half-life of only 21 minutes.

$^{227}_{89}Ac \longrightarrow {}^{0}_{-1}e + {}^{227}_{90}Th$ (beta decay)

$^{227}_{89}Ac \longrightarrow {}^{4}_{2}He + {}^{223}_{87}Fr$ (alpha decay)

$^{223}_{87}Fr \longrightarrow {}^{0}_{-1}e + {}^{223}_{88}Ra$ (beta decay)

(Half-life = 21 min)

All these elements are highly reactive and hence do not occur in free state (i.e. native state). Being strongly electropositive elements, these occur in nature in the form of ionic compounds, i.e. exist in combined state as halides, oxides, silicates, borates and nitrates.

Lithium is the 35th most abundant element by weight in the earth's crust (lithosphere) and mainly occurs in the form of silicates:

Spodumene	$LiAl(SiO_3)_2$ or $LiAl\ Si_2O_6$
Lepidolite	$Li_2Al_2(SiO_3)_3(FOH)_2$

Sodium and potassium are the seventh and eighth most abundant elements by weight in the earth's crust. NaCl and KCl occur in large amounts in sea water. Some important minerals of sodium are as follows:

Rock salt	NaCl
Borax	$Na_2B_4O_7\cdot 10H_2O$
Saltpetre	$NaNO_3$
Mirabilite	Na_2SO_4
Trona	$Na_2CO_3\cdot NaHCO_3\cdot 2H_2O$

Potassium mainly occurs as:

Sylvite or Sylvine	KCl
Sylvinite	Mixture of KCl and NaCl
Carnallite	$KCl\cdot MgCl_2\cdot 6H_2O$

Soluble potassium salts are collectively called *potash*.

There is no convenient source of rubidium. Only one source of caesium is present. These elements are obtained as by-products from lithium processing.

ILLUSTRATION 4.1

How many water molecules of crystallisation are present in (a) trona, (b) borax and (c) carnallite?

Sol.

Mineral	Formula	Water moles of crystallisation
a. Trona	$Na_2CO_3\cdot NaHCO_3\cdot 2H_2O$	2
b. Borax	$Na_2B_4O_7\cdot 10H_2O$	10
c. Carnallite	$KCl\cdot MgCl_2\cdot 6H_2O$	6

4.4 GENERAL TRENDS IN ATOMIC AND PHYSICAL PROPERTIES

All the alkali metals exhibit a striking resemblance in their physical and chemical properties with increasing atomic numbers due to their similar electronic configuration.

The trends obtained in the variation of different atomic and physical properties are given in Table 4.1.

4.4.1 Electronic Configuration

The electronic configuration of alkali metals consists of a noble gas core with a single valence electron in *ns*-orbital (Table 4.2). Therefore, the general electronic configuration of alkali metals is ns^1 (where n = 2–7). Since all the alkali metals have identical configuration, ns^1 in their valence shell, they have similar physical and chemical properties.

4.4.2 Atomic and Ionic Radii

Statement: The atoms of alkali metals have the largest size in their respective periods. The atomic radii increases down the group (↓) among the alkali metals (Table 4.1).

Explanation: In alkali metals, there is only one electron in the outermost shell and the noble gas core shields this electron quite effectively from the nuclear charge.

Table 4.1 Atomic and physical properties of alkali metals

Properties	Lithium	Sodium	Potassium	Rubidium	Caesium	Francium
Symbol	Li	Na	K	Rb	Cs	Fr
Atomic number	3	11	19	37	55	87
Atomic mass (g mol^{-1})	6.94	22.99	39.10	85.47	132.91	(223)
Electronic configuration	$[He]2s^1$	$[Ne]3s^1$	$[Ar]4s^1$	$[Kr]5s^1$	$[Xe]6s^1$	$[Rn]7s^1$
Crystal structure	*bcc*; *hcp* (at low temperature)	*bcc*	*bcc*	*bcc*	*bcc*	*bcc*
Metallic radii (pm)	152	186	227	248	265	—
Covalent radii (pm)	123	157	203	216	235	—
Ionic radii, M^+(pm)	76	102	138	152	162	(180)

Properties	Lithium	Sodium	Potassium	Rubidium	Caesium	Francium
Ionisation enthalpy IE_1 (kJ mol^{-1})	520	496	419	403	376	375
IE_2 (kJ mol^{-1})	7297	4560	2930	2655	2420	—
Electronegativity (Pauling)	1.0	0.9	0.8	0.8	0.7	—
Melting point (K)	454	371	336	312	302	—
Boiling point (K)	1615	1156	1032	961	944	—
Density (g cm^{-3})	0.53	0.97	0.86	1.53	1.90	—
Colour of flame	Crimson red	Yellow	Violet	Red violet	Blue	—
Hydration enthalpy (kJ mol^{-1})	–506	–406	–330	–310	–276	—
Hydrated radii $M^{\oplus}$(aq)/(pm)	340	276	232	228	276	—
Ionic mobility at infinite dilution or ionic conduction	33.5	43.5	64.5	67.5	68.0	—
E° (V)	–3.04	–2.714	–2.925	–2.930	–2.927	
Abundance in lithosphere (ppm)	18	22700	18400	78	2.6	—
Relative abundance	35	7	8	23	46	—

Table 4.2 Electronic configuration of alkali metals

Element		Electronic configuration
Lithium (Li)	Z = 3	[He]$2s^1$
Sodium (Na)	Z = 11	[Ne]$3s^1$
Potassium (K)	Z = 19	[Ar]$4s^1$
Rubidium (Rb)	Z = 37	[Kr]$5s^1$
Caesium (Cs)	Z = 55	[Xe]$6s^1$
Francium (Fr)	Z = 87	[Rn]$7s^1$

Due to small effective nuclear charge experienced by the valence shell electron, the atoms of alkali metals have the largest size in their respective periods.

Down the group (↓), as the atomic number increases, there is a progressive addition of one new energy shell at every step. As a result, the screening effect caused by the inner-filled shells on the valence *s* electron increases and electron cloud tends to expand. In other words, the force of attraction between the nuclei and valence shell electron decreases due to the increase in screening effect, resulting in an increase in the atomic size

However, along the period (→) with an increase in the atomic number, nuclear charge also increases. This leads to decrease in the atomic radii because of the increase in the force of attraction between the nuclei and the valence shell electron. But the effect of increase in the screening effect is more predominant as compared to the effect of increase in nuclear charge and hence the atomic radii of alkali metals increase from lithium to caesium.

Li < Na < K < Rb < Cs

Alkali metals change into positively charged ion by losing their lone valence shell electron. Within the group, the ionic radii increase with an increase in atomic numbers.

Statement: The ionic radii are much smaller as compared to the atomic radii of the corresponding atom.

Explanation: This can be explained as follows:

- When the valence shell electron (ns^1) is removed to get unipostive ion ($M^{\oplus}$), the cation formed has one shell less than the corresponding atom.
- With the loss of valence shell electron, the effective nuclear charge, Z* or Z_{eff} increases, which leads to an increased force of attraction between nuclei and remaining electrons, resulting in further decrease in the radii.

  Hence, positive ions or cations are always smaller than the parent atom ($M^{\oplus} < M$).

4.4.3 Crystal Structure

In the solid state, alkali metals normally adopt body-centred cubic (*bcc*) structure in which the metal atoms are surrounded by eight equidistant neighbours, although at low temperatures lithium forms hexagonal closed packed (*hcp*) structure. The Li atoms in each layer have six neighbours in the same place arranged at the corners of a regular hexagon; alternate layers are staggered relative to each other, so that any one lithium atom also has three near neighbours in both the adjacent layers giving a coordination number of 12 to Li.

4.4.4 Ionisation Energy or Enthalpy

Statement: The first ionisation energy of alkali metals is quite low as compared to the elements of other groups belonging to the same period.

Explanation: The atoms of the alkali metals are the largest in their respective periods. Therefore, the single electron present in the outermost shell (ns^1) is far away from the nucleus and is effectively shielded by the electrons present in the noble gas core. Hence, the valence shell electron experiences less force of attraction from the nucleus and hence can be easily removed by providing a small amount of energy.

$$M_{(g)} \longrightarrow M^{\oplus}_{(g)} + e^{\ominus}$$

Statement: The ionisation energy of the alkali metals decreases down the group (↓), from Li to Cs.

Explanation: The ionisation energy decreases down the group (↓), i.e.

Li > Na > K > Rb > Cs.

The decrease in the ionisation energy is due to the increase in the size of alkali metals and the increase in the magnitude of the screening effect is due to the increase in the number of intervening electrons (i.e. the electrons present in between the nucleus and valence shell electron). As a result, the force of attraction between nucleus and valence shell electron decreases, hence the ionisation energy decreases.

Statement: The second ionisation energy of alkali metals is quite high.

Explanation: After the removal of the first electron, the resulting monovalent cation formed has noble gas configuration. For example,

$$\underset{[Ne]3s^1}{Na} \xrightarrow[-e^{\ominus}]{+IE_1} \underset{\substack{[Ne] \\ \text{Stable noble gas configuration}}}{Na^{\oplus}}$$

The second electron has to be removed from noble gas core, which is highly stable and thus requires larger amount of energy. Thus, the second ionisation energy of alkali metals is quite high. *Hence, in great majority of their compounds, alkali metals exist as unipositve ions*. The second ionisation energy of alkali metals, like the first ionisation energy, also deceases down the group (↓).

4.4.5 Electropositive Character

Statement: Alkali metals are highly electropositive and their electropositivity increases from Li to Cs.

Explanation: On account of their low ionisation energies, alkali metals have a strong tendency to lose their valence electron and are strongly electropositive.

$$M_{(g)} \longrightarrow M^{\oplus}_{(g)} + e^{-}$$

Since the ionisation energy decreases down the group (↓), the tendency to lose the valence shell electron increases down the group (↓) and hence the electropositive character increases from Li to Cs:

Electropositive character: Li < Na < K < Rb < Cs

Caesium is the most electropositive element.

4.4.6 Metallic Character

Statement: Alkali metals are typical metals and the metallic character increases down the group (↓).

Explanation: The metallic character of an element is its tendency to lose the valence electron and form cation.

$$M \longrightarrow M^{\oplus} + e^{\ominus}$$

Due to the low ionisation energy, alkali metals have a strong tendency to lose the valence electron and hence are typical metals. Down the group (↓), the ionisation energy decreases, i.e. the tendency to lose the valence electron increases and hence the metallic character increases from Li to Cs:

Li < Na < K < Rb < Cs

4.4.7 Oxidation State

Statement: Alkali metals exhibit +1 oxidation state in their compounds.

Explanation: On account of the low ionisation energy of alkali metals, they have a strong tendency to lose their single valence electron (ns^1) and change into unipositive ion.

$$\underset{[\text{Noble gas}]\,ns^1}{M} \longrightarrow \underset{[\text{Noble gas}]}{M^{\oplus} + e^{\ominus}} \qquad \underset{[Ne]3s^1}{Na} \longrightarrow \underset{[Ne]}{Na^{\oplus} + e^{\ominus}}$$

By losing the solitary valence electron, alkali metals acquire the stable configuration of the nearest noble gas. Therefore, these elements have a strong tendency to form $M^{\oplus}$ ion in their compounds and thus exhibit an oxidation state of +1 and form ionic compounds.

After the removal of the first electron, alkali metals acquire noble gas configuration which is highly stable. The second electron has to be removed from the noble gas core, and thus, the second ionisation energy is quite high and is not available under the conditions of the formation of chemical bonds. Hence, alkali metals do not form M^{2+} ion in any of their compounds. Alkali metals are thus univalent and form ionic compounds.

4.4.8 Electronegativity

Statement: The electronegativity values of alkali metals are very low.

Explanation: This is because of the fact that the outermost orbit is a long way from the nucleus and the effective nuclear charge on them is low, i.e. alkali metals have very less tendency to gain an electron.

Statement: The value of electronegativity decreases from lithium to caesium.

Explanation: On moving down the group (↓), from lithium to caesium, because of the increase in size and thereby the decrease in effective nuclear charge, the tendency to gain an electron decreases and hence electronegativity decreases from lithium to caesium. Thus,

Li < Na < K < Rb < Cs

4.4.9 Physical Properties

Some of the characteristic physical properties of alkali metals are as follows:

- Alkali metals are soft in nature (except lithium) and can be easily cut with a knife.
- They have silvery lustre.
- They are malleable and ductile.
- They are good conductors of electricity.
- They are good conductors of heat (thermal conductivity).
- Alkali metals exhibit photoelectric effect.
- Alkali metals have low melting and boiling points.
- Alkali metals have low density.

All the above-mentioned properties increase from Li to Cs and can be explained on the basis of **metallic bonding.**

Explanation: A theory, known as the *electron pool* or *electron gas* or *electron cloud theory*, was proposed by Drude (1900) and later on developed by Lorentz (1916) to explain metallic bond, i.e. the nature of forces holding the metal atoms together in a metal lattice or crystal.

Since metals have low ionisation energies, they easily lose their valence electrons to form metal ions, also known as *positive cores* or *kernels*. These free electrons move through the empty space in closed packed metal ions and are shared simultaneously by all the atoms together by a characteristic type of bond known as the *metallic bond*. The free electrons now belong to the crystal as a whole and not to any individual metal atom. Due to the delocalisation of electrons, the kernels remain fixed in the crystal lattice while the delocalised electrons move freely in the vacant valence orbitals.

Thus, on the basis of this theory, a metal is considered to be a group of kernels or positive metal ions packed together as closely as possible in a regular geometric pattern and immersed in a sea of electrons, called *electron pool* or *electron gas* or *electron cloud*, which move about freely in vacant valence orbitals.

The force of attraction that binds the metal ions to free electrons is called the *metallic bond*, and this force of attraction holds the atoms together.

Down the group (↓), as the size of the metal atom increases, the force of attraction that binds the metal ions to valence electrons decreases. The repulsive force between positive metal ions increases due to the increase in the number of non-bonding electrons. As a result, the forces holding atoms or ions together in a lattice structure decrease and the metallic bond strength decreases.

Li < Na < K < Rb < Cs

4.4.9.1 Nature of Alkali Metals

Mentioned below are the explanations of the above-mentioned physical properties of the alkali metals.

Statement: Alkali metals are soft in nature and can be easily cut with a knife.

Explanation: Since alkali metals have large size and single electron in the valence shell, metallic bonding is weak. As a result, alkali metals are soft and can be easily cut with a knife. As the metal lattice is changed from Li to Cs, due to decrease in the force of attraction between positive metal ion and freely moving electron, the strength of the metallic bond decreases from Li to Cs, i.e. Li is the hardest of all the alkali metals and cannot be cut with a knife. Because of the continuous decrease in the metallic bond strength, on account of increase in atomic size, the softness increases with increase in atomic number.

4.4.9.2 Metallic Lustre

Statement: Alkali metals have silvery lustre.

Explanation: This can be explained on the basis of highly mobile electrons of metal lattice. When a light beam comprising photons strikes the metal surface, the energy of photons ($E = h\nu$) interact with electrons on the surface and make them oscillate. Like any other moving charged object, these moving electrons emit electromagnetic radiations in the form of light. This light appears to be reflected from the surface of the metal, and hence the metal appears to have silvery lustre.

4.4.9.3 Malleable or Ductile

Statement: Alkali metals are malleable/plastic and ductile.

Explanation: Alkali metals are *malleable*, i.e. when they are beaten by a hammer, they get converted into sheets. They are *ductile* as well, i.e. when they are drawn through a die, they are converted into thin wires.

When a metal is beaten, one layer of positive metal ions moves along another layer through a distance and occupies a new position. Since the valence electrons forming the sea of electrons are mobile, they also move along with the positive metal ions and thus the structure of the metal is retained and the crystal structure is restored (Fig. 4.1). This results in the reduced thickness of the metal or the metal is converted into thin sheet or thin wires.

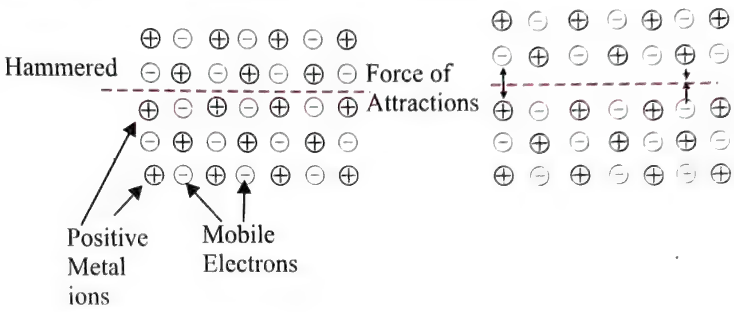


Fig. 4.1 Explanation of malleability and ductility of metals

The malleability and ductility decrease from Li to Cs, due to decrease in the metallic bond strength from Li to Cs.

4.4.9.4 Electrical Conductivity

Statement: Alkali metals are good conductors of electricity, and electrical conductivity increases from lithium to caesium.

Explanation: The valence electrons form a sea of electron cloud which is spread throughout the lattice. Since these electrons are not fixed, thus when the electric field is applied, they can move freely throughout the lattice. The metals therefore are good conductors of electricity. Down the group (↓), since the strength of metallic bond decreases, i.e. the force of attraction between positive metal ions and valence electrons decreases, therefore the electrical conductivity increases from Li to Cs.

Electrical conductivity: Li < Na < K < Rb < Cs

4.4.9.5 Thermal Conductivity

Statement: Alkali metals are good conductors of heat (thermal conductivity) and thermal conductivity increases from lithium to caesium.

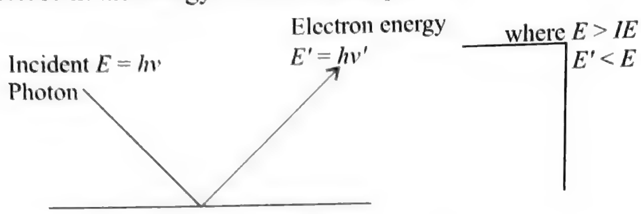
Explanation: Thermal conductivity can be explained on the basis of mobile electrons present in the metal lattice. When a piece of metal is heated at one end, the free electrons absorb heat energy and move rapidly through the metallic lattice towards the cooler end. During this process, they collide with adjacent electrons and transfer their heat energy to them; and thus act as a good conductor of heat. Thermal conductivity also increases down the group (↓) due to the decrease in the strength of metallic bond strength.

Thermal conductivity: Li < Na < K < Rb < Cs.

4.4.9.6 Photoelectric Effect

Statement: Alkali metals (except lithium) exhibit photoelectric effect.

Explanation: When a light beam, comprising photons strike the metal surface, the photons are completely absorbed by the surface and transfer their energy ($E = h\nu$) to the electrons on the surface. If the energy of the photon exceeds the ionisation energy of the metal, an electron is ejected from the surface along with a resultant decrease in the energy of the incident photon.



This phenomenon of ejection or emission of electrons from the metal surface when a beam of light having energy greater than the ionisation energy of metal is allowed to fall on the surface of metal is called *photoelectric effect*. The electrons that are emitted from the surface are called *photoelectrons*. The energy of photoelectrons is less than the energy of incident photons.

Since alkali metals have low ionisation energy, when light beam strikes the metal surface, even the low energy photons easily eject electrons, especially in potassium and caesium. That is why alkali metals exhibit photoelectric effect. Therefore, alkali metals, especially caesium, can be used in photoelectric cells. Since lithium has the highest ionisation energy among the alkali metals, it does not show the phenomenon of photoelectric effect.

4.4.9.7 Melting and Boiling Points

Statement: Alkali metals have low melting and boiling points. Both melting points and boiling points decrease down the group (↓).

Explanation: The low melting point is attributed to the larger atomic size of the alkali metals, due to which the binding energy of their atoms in crystal lattice are low. Further, on moving down the group (↓), their atomic size increases and the strength of the metallic bond decreases, which causes decrease in melting points: Li < Na < K < Rb < Cs.

The boiling points of alkali metals also follow the same order due to the same reasons.

4.4.9.8 Density

Statement: The densities of alkali metals are low and increase in different down the group (↓).

Explanation: The low density is attributed to the large atomic size and weak metallic bond of alkali metals. Down the group (↓), from Li to Cs, both atomic size and atomic mass increase. But the corresponding increase in the atomic mass is not compensated by the increase in atomic volume. Hence, the ratio of atomic mass/atomic volume, i.e. density, gradually increases (Table 4.3).

Table 4.3 Density of alkali metals

	Li	Na	K	Rb	Cs
Density (g cm^{-3})	0.53	0.97	0.86	1.53	1.90
		Exception			

Statement: The density of potassium is lower than that of either sodium or rubidium.

Explanation: This can be explained on the basis of disproportionately larger metallic radius of potassium. At potassium, $3d$ and $4s$ have almost the same energy. Hence, the $4s^1$ electron is free to move to $3d$-orbital leading to an expansion in the size of the atom. Potassium atom has a metallic radius much nearer to that of rubidium than to sodium. Since the alkali metals are all of similar crystal structure (bcc), the disproportionately larger size or volume of potassium atoms corresponds to the low density of potassium.

Lithium is the lightest metal having a density of 0.534 g cm^{-3}. It cannot be stored in kerosene oil because it floats on the surface. It is kept wrapped in paraffin wax.

4.4.10 Flame Colouration

Statement: Alkali metals or their salts impart a characteristic colour to the Bunsen flame.

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Yellow	Violet	Red violet	Blue
λ (nm)	670.8	589.2	766.5	780.0	455.0

Explanation: When alkali metals or their salts are heated in the Bunsen flame, they absorb energy from the flame and the outermost electron gets excited to higher energy levels. When the excited electrons fall back to their original energy level, the excess energy is emitted in the form of electromagnetic radiation ($E = h\nu$) which falls in the visible region, thereby imparting colour to the flame. When exposed to the same source of energy (i.e. the Bunsen flame) due to the difference in ionisation energies, the outermost electron in different atoms will be excited to different energy levels, i.e. the outermost electron in the atom having higher ionisation energy is excited to lower level than an atom having lower ionisation energy. Thus, the frequency of radiation which depends upon the amount of energy ($E = h\nu$) will be different for different elements, i.e. different elements will impart characteristic colour to the Bunsen flame.

The colour actually arises from the electronic transitions in short-lived species which are formed momentarily in the flame. The flame is rich in electrons and, in case of sodium, the ions are temporarily reduced to atoms.

$$Na^{\oplus} + e^{\ominus} \longrightarrow Na$$

The sodium D-line (which is actually a doublet at 589.0 nm and 589.6 nm) arises from the electronic transition $3s^1 \rightarrow 3p^1$ in sodium atoms formed in the flame. The colours from different elements do not arise from the same transition or from the same species. Thus, the red line for lithium arises from a short-lived LiOH species formed in the flame.

4.4.11 Hydration Energy or Enthalpy and Radii of Hydrated Ion

Statement: The hydration enthalpy of the alkali metal ions decreases with the increase in ionic size from $Li^{\oplus}$ ion to $Cs^{\oplus}$ ion.

Explanation: The hydration enthalpy is the amount of energy released when one gram mole of a gaseous ion is dissolved in water.

$$M^{\oplus}_{(g)} + xH_2O \longrightarrow [M(H_2O)_x]^{\oplus} + \text{Hydration enthalpy}$$

The phenomenon of hydration can be explained in terms of Lewis acid–Lewis base interaction, i.e. water molecule donates an electron pair (Lewis base) to the metal ion (Lewis acid), thus forming a complex. This interaction results in the evolution of energy known as *hydration enthalpy* or *hydration energy* hence the hydration of ions is an exothermic process.

Some water molecules touch the metal ion directly and bond to it by means of coordinate bond, thus forming a complex. These water molecules constitute *primary hydration sphere* or *primary shell of water*. In the primary shell, $Li^{\oplus}$ ion is tetrahedrally surrounded by four water molecules forming $[Li(H_2O)_4]^{\oplus}$. sp^3 hybridisation (tetrahedral).

Due to the unavailability of low lying *d*-orbitals, lithium cannot expand its coordination number beyond four and hence $[Li(H_2O)_4]^{\oplus}$ is formed.

In other cases, due to the availability of low lying *d*-orbitals, higher coordination number is achieved, i.e. $[M(H_2O)_6]^{\oplus}$ is formed, e.g. $[K(H_2O)_6]^{\oplus}$ d^2sp^3 hybridisation (octahedral geometry)

Because the water molecules in the primary hydration sphere are associated with a cation, they have strong tendency to further form the hydrogen bond with other water molecules, thus forming secondary hydration sphere. Secondary hydration sphere thus further hydrates the $[M(H_2O)_x]^{\oplus}$ ion, though these are held by weak ion–dipole attractive forces (Fig. 4.2). The strength of these forces is inversely proportional to the size of the metal ion.

Thus, the secondary hydration decreases from lithium to caesium and therefore $Li^{\oplus}$ ion in aqueous medium is the most heavily hydrated ion, while $Cs^{\oplus}$ ion is the least hydrated ion.

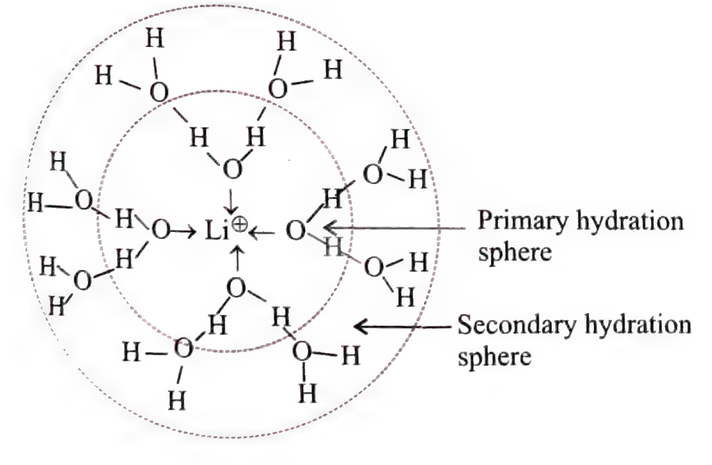


Fig. 4.2 Hydrated $Li^{\oplus}$ ions

Degree of hydration depends on the (i) size of the ion and (ii) charge.

On moving down the group, charge density (charge/radius ratio) decreases and hence the degree of hydration and hence the hydration energy decreases from $Li^{\oplus}$ ion to $Cs^{\oplus}$ ion.

Degree of hydration is

$$Li^{\oplus}_{(aq)} > Na^{\oplus}_{(aq)} > K^{\oplus}_{(aq)} > Rb^{\oplus}_{(aq)} > Cs^{\oplus}_{(aq)}$$

Hence the radii of hydrated ion decrease from $Li^{\oplus}$ to $Cs^{\oplus}$.

$$Li^{\oplus}_{(aq)} > Na^{\oplus}_{(aq)} > K^{\oplus}_{(aq)} > Rb^{\oplus}_{(aq)} > Cs^{\oplus}_{(aq)}.$$

4.4.12 Electrical Conductivity in Aqueous Solution

Statement: In their aqueous solution, alkali metal salts conduct electricity. $Li^{\oplus}$ ion, being the smallest ion, is expected to conduct electricity better than other larger ions, but the observed conductivity is in the order:

$$Li^{\oplus}_{(aq)} < Na^{\oplus}_{(aq)} < K^{\oplus}_{(aq)} < Rb^{\oplus}_{(aq)} < Cs^{\oplus}_{(aq)}$$

Explanation: This trend in conductivity is due to the fact that ions are hydrated in solution.

The degree of hydration is directly proportional to charge density (charge/radius ratio). Although the size of $Li^{\oplus}$ ion is smallest, the size of hydrated ion is the largest. The size of the hydrated ions decreases from $Li^{\oplus}$ to $Cs^{\oplus}$, i.e.

$$Li^{\oplus}_{(aq)} > Na^{\oplus}_{(aq)} > K^{\oplus}_{(aq)} > Rb^{\oplus}_{(aq)} > Cs^{\oplus}_{(aq)}$$

As the size of the ion decreases, the mobility or movement of ions under the effect of electric current increases and hence the electrical conductivity in aqueous solution increases from $Li^{\oplus}_{(aq)}$ to $Cs^{\oplus}_{(aq)}$.

Electrical conductivity or ionic mobility at infinite dilution is :

$$Li^{\oplus}_{(aq)} < Na^{\oplus}_{(aq)} < K^{\oplus}_{(aq)} < Rb^{\oplus}_{(aq)} < Cs^{\oplus}_{(aq)}.$$

4.4.13 Reducing Property

A reducing agent (atom ion or molecule) is a substance which reduces some other substance and itself gets oxidised to a higher valency state by losing one or more electrons.

Statement: Alkali metals act as strong reducing agents.

Explanation: Due to their low ionisation energy values, alkali metals have a strong tendency to lose their valence electron (ns^1) and hence they act as strong reducing agents.

$$M \longrightarrow M^{\oplus} + e^-$$

The tendency of alkali metals to act as a strong reducing agent is evident from the fact that alkali metals can liberate H_2 when they react with water and acids.

$$2M + 2H_2O \longrightarrow 2MOH + H_{2(g)}$$

$$2M + 2HCl \longrightarrow 2MCl + H_{2(g)}$$

The reducing tendency is measured in terms of standard electrode reduction potentials ($M^{\oplus} + e^- \rightleftharpoons M; E^{\ominus}$). These elements have high negative values of reduction potentials, as given in table.

Statement: Despite the fact that lithium has the least tendency to lose the valence electron, it acts as the strongest reducing agent among alkali metals.

Explanation: This statement can be explained on the basis of the fact that in a reduction reaction, other energy terms are also involved besides ionisation energy. Whereas the ionisation energy is only a measure of the conversion of neutral gaseous atom to the gaseous ion,

$$M_{(g)} \longrightarrow M^{\oplus}_{(g)} + e^-$$

The reducing action of alkali metals in aqueous solution is represented by

$$M_{(s)} \longrightarrow M^{\oplus}_{(aq)} + e^-$$

The process can be visualised to involve the following steps:

1. Sublimation of $M_{(s)}$:

$$M_{(s)} \xrightarrow{\Delta_{sub}H^{\ominus}} M_{(g)}$$

This is an endothermic process.

2. Ionisation of $M_{(g)}$:

$$M_{(g)} \xrightarrow{IE_1} M^{\oplus}_{(g)}$$

This is also an endothermic process but Li has the highest IE, while Cs has least IE

3. Hydration of the cation $M^{\oplus}_{(g)}$:

$$M^{\oplus}_{(g)} + H_2O \longrightarrow M^{\oplus}_{(aq)} \qquad \Delta_{hyd}H^{\ominus} = -ve$$

$Li^{\oplus}$ ion being the smallest in size has the highest charge density and gets hydrated to the maximum. Hence, $Li^{\oplus}$ ion has the maximum hydration enthalpy value and this value decreases from lithium to caesium.

The reducing character of the metal ion, i.e. the reduction potential depends on the sum of the three enthalpy terms, i.e. sublimation enthalpy, ionisation enthalpy and hydration enthalpy.

Although the ionisation enthalpy of Li is the highest of all the alkali metals, its hydration enthalpy released is so high that it compensates more than for the high ionisation enthalpy required. Hence, lithium in aqueous solution is the strongest reducing agent ($E^{\ominus} = -3.04$ V).

The reducing power increases from Na to Cs in accordance with the decrease in ionisation enthalpy values.

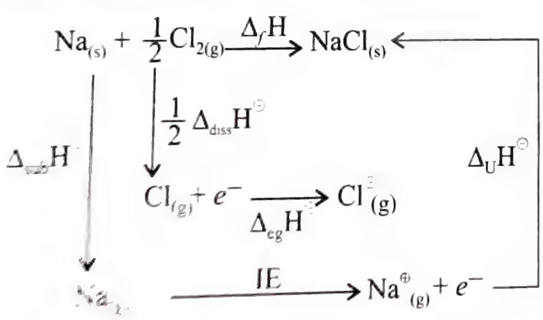
Reducing character: Li > Cs > Rb > K > Na

4.4.14 Nature of the Compounds Formed

Statement: Alkali metals form ionic compounds.

Explanation: Alkali metals have loosely bound (ns^1) electron and this can be removed very easily to form $M^{\oplus}$ ion and that is why alkali metals have highly electropositive character. Because of this, alkali metals readily react with elements having high electronegativity and form ionic compounds.

Ionic compounds are formed because their heat of formation is negative. The reaction between sodium and chlorine takes place with the evolution of 395.8 kJ for each mole of sodium chloride formed. The reaction may be broken down theoretically into a cycle of fundamental energy processes such that the total energy in the cycle is equal to the heat of formation of sodium chloride **(Born–Haber cycle).**



$$\Delta_f H = \Delta_{sub}H + \frac{1}{2}\Delta_{diss}H^{\ominus} + IE + \Delta_{eg}H^{\ominus} + \Delta_U H^{\ominus}$$

[illegible] compounds of alkali metals are purely ionic in nature. [illegible] the liquid metals, though predominantly [illegible] contains a small proportion of dimer molecules. [illegible] studies show the presence of σ-bond between two [illegible] weaker than the corresponding bond in H_2 [illegible]

[illegible] forces arising between the inner shell [illegible] the two atoms.

2. The diffuse nature of outer *ns* orbital resulting in poor overlap.

The strength of the bond in dimers will decrease from Li to Cs because both the above factors increase with the increasing size of the alkali metals.

Statement: The compounds formed by the alkali metals are colourless and diamagnetic.

Explanation: Alkali metal ions have noble gas configurations in which all the electrons are paired. Thus promoting an electron in alkali metal ion requires energy to:

- unpair the electron
- break full shell of electrons
- promote the electron to a higher level

The total energy required is very high and it is due to this fact that the electronic transitions within the metal ion cannot take place by the visible light, and the compounds are typically white. Any transition which occurs will be of high energy and will appear in the UV region rather than in the visible region and will not be visible to the human eye.

Compounds of alkali metals are typically white, except where the colour is the property of anion as in potassium dichromate ($K_2Cr_2O_7$, orange), sodium chromate (Na_2CrO_4, yellow), potassium permanganate ($KMnO_4$, purple). In these compounds, colour is due to the anions $Cr_2O_7^{2-}$, CrO_4^{2-}, $MnO_4^{\ominus}$ and not because of alkali metal ions.

When alkali metals form compounds, all the electrons are paired and hence alkali metal compounds are diamagnetic (except superoxides).

4.4.15 Solubility

Statement: Alkali metal salts (except lithium) are soluble in polar solvents and insoluble in non-polar solvents.

Explanation: Alkali metal salts (except Li) are ionic in nature and hence soluble in polar solvents such as water, liquid ammonia etc. and insoluble in non-polar solvents. This can be explained as follows:

1. Polar solvents have high dielectric constants. The electrostatic forces of attraction between cations and anions in an ionic solid are reduced by the high value of *dielectric constant* of the polar solvent. As a result, the ions move freely and interact with solvent molecules to form solvated ions, and thus ionic salts are soluble in polar solvents.

   Whereas the non-polar solvents cannot reduce the electrostatic force of attraction between cations and anions in the ionic solids and thus ionic solids are insoluble in non-polar solvents.

   Dielectric constant (∈): It is the measure of a substance's ability to separate charges from each other. It is taken as a measure of solvent polarity. Higher dielectric constants mean higher polarity and greater tendency to stabilise charges.

2. Another way of explanation is by taking an example of polar solvent, e.g. water $\left(\overset{\delta-}{O}\text{ with } H_{\delta+}\, H_{\delta+}\right)$ where oxygen is the negative end and hydrogen is the positive end; the negative end of

water molecule interacts with the positive ion (cation) of the ionic solid and the positive end of water molecule interacts with the negative ion (anion) of the ionic solid. For example, consider the dissolution of NaCl in H_2O (Fig. 4.3).

The interaction between ionic solid and polar solvent molecules decreases the energy of the system and reduces the force of attraction between the cations and anions of the ionic solid, and consequently the ions get solvated and the ionic compound dissolves in the polar solvent.

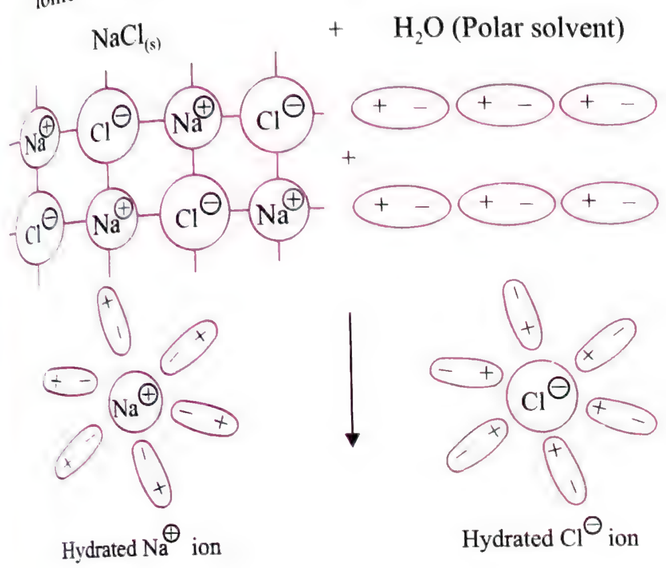


Fig. 4.3 Dissolution of NaCl in water

3. Solubility of ionic solid in polar solvent can also be explained on the basis of relative values of lattice energy and hydration energy.

Ionic solid is soluble in polar solvent when the lattice energy of the compound is overcome by the solvation energy (or hydration energy), if water is solvent. That is,
Lattice energy of compound < Solvation energy

The process of dissolution of alkali metal salts in a polar solvent involves:

a. Separation of ionic compound, $MX_{(s)}$, into their constituent ions in the gaseous state, namely $M^{\oplus}_{(g)} + X^{\ominus}_{(g)}$ which make up the lattice.

$$MX_{(s)} \xrightarrow{\Delta_u H^{\ominus}} M^{\oplus}_{(g)} + X^{\ominus}_{(g)}$$

The energy required for this process is called *lattice energy*.

b. The ions formed in step (a) get solvated (or hydrated). The cations are attached to the negative end of the dipolar water molecules. The positive pole of water molecules points towards the anion. The cations being smaller as compared to anions, the interaction between a water molecule and a cation is much stronger than that between a water molecule and an anion. These interactions result in the evolution of energy which is known as *solvation energy* (or hydration energy).

$$M^{\oplus} + x(\text{solv}) \longrightarrow [M(\text{solv})_x]^{\oplus} \quad \Delta_{hyd}H^{\ominus} = -ve$$

$$X^{\ominus} + y(\text{solv}) \longrightarrow [X(\text{solv})_y]^{\ominus} \quad \Delta_{hyd}H^{\ominus} = -ve$$

In general, an ionic solid will be soluble in polar solvent if the hydration or solvation energy overcome the lattice energy of the compound, which is responsible for holding the ions together in an ionic crystal.

Non-polar or slightly polar solvents cannot exert the necessary attractive force on the ions in the lattice, with the result that appreciable amounts of ionic compounds do not dissolve in them.

ILLUSTRATION 4.2

On addition of conc HNO_3 to the aqueous solution of common salt, sodium chloride crystallises out. Give reason.

Sol. Aqueous sodium chloride solution contains

$$NaCl(s) + H_2O \rightarrow \underset{\text{Hydrated sodium ion}}{[Na(H_2O)_x]^{\oplus}} + \underset{\text{Hydrated chloride ion}}{[Cl(H_2O)_y]^{\ominus}}$$

On addition of conc HNO_3, the reaction between hydrated ions and conc HNO_3 takes place, thereby water molecules which were previously forming hydrated species are removed. The ions are thus unsolvated and hence reform the crystal lattice resulting in the crystallisation of sodium chloride (NaCl).

ILLUSTRATION 4.3

Why formation of Na^{2+} ion is not possible?

Sol. $$\underset{1s^2 2s^2 2p^6 3s^1}{Na} \xrightarrow[-e^{\ominus}]{+IE_1} \underset{1s^2 2s^2 2p^6}{Na^{\oplus}} \xrightarrow[-e^{\ominus}]{+IE_2} \underset{1s^2 2s^2 2p^5}{Na^{2+}}$$

After formation of $Na^{\oplus}$, the $Na^{\oplus}$ ion has attained stable noble gas configuration and hence further removal of electrons will require high energy.

ILLUSTRATION 4.4

Both sodium and potassium are present in equal abundance in the earth's crust, but sodium is about 30 times as abundant as potassium in oceans. Give reasons.

Sol. As compared to sodium, potassium is larger in size. Therefore, potassium salts with large anions are less soluble and are thus retained behind, while more soluble sodium salts are carried to the sea. Also potassium is strongly bound with complex silicates and aluminosilicates in the soil and are thus retained. Potassium ions are preferentially absorbed by plants whereas sodium ions proceed to the sea.

ILLUSTRATION 4.5

Give reasons for the following:

a. Alkali metals do not occur free in nature.
b. Alkali metal salts impart characteristic colour to the flame.
c. Caesium is used in photoelectric cell.
d. Alkali metals are good reducing agents in aqueous medium.

Sol.

a. Alkali metals are highly reactive because of their large size and low ionisation enthalpy values and hence they do not occur free in nature. They readily combine with oxygen, moisture and carbon dioxide present in air.

b. When alkali metal salts are heated in the Bunsen flame, they absorb energy. The valence shell electron gets excited to higher energy level. When the exited electron returns to its original energy level, excess energy is emitted in the form of electromagnetic radiation which falls in the visible region, thereby imparting colour to the flame.

Since the ionisation energy dsecreases from Li to Cs, the amount of energy released increases from Li to Cs. Thus, the frequency of light emitted increases in accordance with the formula $E = h\nu$. Hence, different alkali metals impart characteristic colour to the flame.

c. Because of low ionisation enthalpy, caesium is used in photoelectric cells, since low-energy photons (light) can eject electron(s) from the surface.

d. Alkali metals are good reducing agents because they can lose electron(s) easily on account of low ionisation enthalpy values.

ILLUSTRATION 4.6

Give reasons for the following:

a. Alkali metals are soft and volatile.

b. First ionisation enthalpies of alkali metals are low.

Sol.

a. Alkali metals have only one valence electron per metal atom. The binding energies in the closed packed metal lattice are weak. That is why alkali metals are soft and volatile.

b. Alkali metals have large size and thus the valence shell electron (ns^1) is loosely bound and can be removed easily by providing low amount of energy. That is why the first ionisation enthalpies of alkali metals are low.

$$M_{(g)} \xrightarrow{IE_1} M^{\oplus}_{(g)} + e^-$$

ILLUSTRATION 4.7

Explain the following:

a. Despite the fact that $Li^{\oplus}$ ion has the smallest size among alkali metals, it moves through a solution less rapidly than the others.

b. LiF has the lowest solubility among group 1 metal halides.

c. The softness of alkali metals increases with the increase in atomic number.

Sol.

a. $Li^{\oplus}$ ion has the highest charge density (charge/radius ratio) and hence it has maximum degree of hydration. As a result, the size of hydrated $Li^{\oplus}$ ion is the largest and it moves less rapidly than the other smaller hydrated alkali metal ions through aqueous solution.

b. LiF has very high lattice energy because of the small size of both $Li^{\oplus}$ and $F^{\ominus}$ ions. This high lattice energy is not compensated by hydration energy of LiF and hence LiF has the lowest solubility of group 1 metal halides.

c. Alkali metals have only one electron per large-sized metal atom and hence the strength of metallic bond is low. Thus, alkali metals are soft in nature . Down the group (↓), as the atomic number increases, the atomic size also increases. This leads to weakening of the strength of metallic bond and hence softness increases.

4.5 CHEMICAL PROPERTIES OF ALKALI METALS

Alkali metals are highly reactive elements. The cause for their high chemical reactivity is due to:

- Large size
- Low ionisation enthalpy
- Low heat of atomisation

As the value of ionisation enthalpy decreases down the group, the reactivity of alkali metals increases from Li to Cs. Some typical reactions of group 1 elements are given in Table 4.4.

Table 4.4 Some typical reactions of group 1 elements

Reaction	Remarks
$4Li + O_2 \longrightarrow 2Li_2O$ $2Na + O_2 \longrightarrow Na_2O_2$ $M + O_2 \longrightarrow MO_2$ (M = K, Rb, Cs)	With excess oxygen, on heating, lithium reacts to form monoxide, sodium forms peroxide, and K, Rb, Cs form superoxide.
$Li + O_2 \longrightarrow Li_2O$ $6Li + N_2 \longrightarrow 2Li_3N$ $M + O_2 \longrightarrow M_2O$ (M = Na, K, Rb, Cs)	With air, Li reacts with aerial O_2 and N_2 to form monoxide and nitride, whereas other alkali metals form only monoxide.
$2M + 2H_2O \longrightarrow$ $2MOH + H_2$	Li is slowly hydrolysed by water, whereas Na reacts vigorously and K, Rb, Cs react explosively forming the corresponding metal hydroxide and liberating H_2 gas. The hydroxides are the strongest bases known.
$2M + H_2 \longrightarrow 2MH$	Ionic salt like hydrides.
$2M + X_2 \longrightarrow 2MX$ (X = F, Cl, Br, I)	All alkali metals react with halogens forming corresponding metal halide.
$6Li + N_2 \longrightarrow 2Li_3N$	Li is the only alkali metal to react with N_2. Reactivity increases with increase in temperature.
$2M + 2C \longrightarrow M_2C_2$	Li and Na react to form acetylides: K, Rb, Cs react with C to give non-stoichiometric compounds.

4.5.1 Reactivity Towards Air

Statement: Alkali metals tarnish in air.

Explanation: Alkali metals tarnish in air due to the formation of oxides (on reaction with oxygen), which in turn react with moisture to form hydroxides. These hydroxides further react with aerial CO_2 to form carbonates.

$$M_{(s)} + O_2 \longrightarrow M_2O_{(s)}$$

$$M_2O_{(s)} + H_2O \longrightarrow 2MOH_{(s)}$$

$$MOH_{(s)} + CO_2 \longrightarrow M_2CO_{3(s)} + H_2O$$

That is why alkali metals are preserved in a hydrocarbon solvent such as kerosene oil which prevents the contact of alkali metal with air.

Statement: When heated in excess of air, lithium forms monoxide (Li_2O), sodium forms peroxide (Na_2O_2) and potassium, rubidium and caesium form superoxides (MO_2, where M = K, Rb or Cs) predominantly.

Explanation: Lithium when heated with oxygen at 200°C forms monoxide

$$Li + O_2 \xrightarrow{200°C} \underset{\text{Lithium monoxide}}{Li_2O} \qquad (2Li^{\oplus} + O^{2-})$$

Sodium when heated with oxygen at 300°C forms peroxide.

$$Na + O_2 \longrightarrow \underset{\text{Sodium peroxide}}{Na_2O_2} \qquad (2Na^{\oplus} + O_2^{2-})$$

Potassium, rubidium and caesium react with oxygen to form superoxide.

$$M + O_2 \longrightarrow MO_2 \text{ (where M = K, Rb, Cs)} \qquad (M^{\oplus} + O_2^{\ominus})$$

The reactivity of alkali metals with oxygen increases down the group. Further, as the size of alkali metal increases, the stability of peroxide or superoxide also increases. This is due to the stabilisation of large anions by large cations because of their high lattice energy.

This can also be explained as follows: $Li^{\oplus}$ ion, because of its small size, has a strong positive field around it which on combination with oxide (O^{2-}) ion restricts the spread of the negative charge (electron cloud) towards another oxygen atom and thus prevents the formation of the O–O bond either in peroxide (O_2^{2-}) or superoxide ($O_2^{\ominus}$).

$Na^{\oplus}$ ion is larger than $Li^{\oplus}$ ion. Hence, the positive field around $Na^{\oplus}$ ion is not strong enough to prevent the formation of $(-O-O-)^{2-}$ in peroxide but is strong enough to prevent the formation of $(O \cdots O)^{\ominus}$ in superoxide ion.

The other alkali metals, namely $K^{\oplus}$, $Rb^{\oplus}$ and $Cs^{\oplus}$ are too large and thus have low positive field around them. This small positive field cannot attract the electron cloud of O=O in oxygen molecule to such an extent that the O–O bond cleaves completely to give O^{2-} ion giving a monoxide. These ions therefore prefer to form superoxides by donating an electron to oxygen molecule.

In all these oxides, the oxidation state of alkali metal is +1.

4.5.2 Reactivity Towards Water

Alkali metals react with water to form their hydroxides and liberate hydrogen gas (H_2).

$$2M + 2H_2O \longrightarrow \underset{\text{Alkali metal hydroxide}}{2NaOH} + H_2\uparrow$$

(M = Li, Na, K, Rb or Cs)

Alkali metals have large negative reduction potential values ($E^{\ominus}$) and thus they are better reducing agents than hydrogen and react with compounds containing acidic hydrogen atoms such as H_2O, alcohols (ROH), acetylene (HC ≡ CH), hydrogen halides liberating hydrogen.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2\uparrow$$

$$2Na + 2ROH \longrightarrow \underset{\text{Sodium alkoxide}}{2NaOR} + H_2\uparrow$$

$$2Na + HC \equiv CH \longrightarrow \underset{\text{Sodium acetylide}}{NaC \equiv CNa} + H_2\uparrow$$

$$2Na + 2HX \longrightarrow \underset{\text{Sodium halide}}{2NaX} + H_2\uparrow$$

Statement: The reaction of alkali metals with water becomes more and more violent down the group (↓), i.e. lithium reacts gently, sodium melts on the surface of water and the molten metal moves around vigorously and sometimes catches fire. Potassium, rubidium and caesium melt and always catch fire.

Thus, lithium is the least reactive while the reactivity of other alkali metals towards the compounds containing acidic hydrogen (e.g. water, alcohol etc.) increases down the group (↓).

Explanation: This is due to the increase in the electropositive character on moving from lithium to caesium. The oxidation potential of lithium is the highest among alkali metals, i.e. free energy $(\Delta G)^{\ominus}$ released will be maximum for lithium.

$$Li \longrightarrow Li^{\oplus} + e^{-}; \qquad E^{\ominus}_{ox} = +3.04$$

$$\Delta G^{\ominus} = -nFE^{\ominus}_{ox}$$

Taking this view into consideration, it looks rather surprising that lithium reacts gently with water whereas potassium, which liberates less energy, reacts violently and catches fire. The explanation lies in the kinetics (i.e. the rate at which the reaction proceeds) rather than in thermodynamics (i.e. the total amount of energy released).

Lithium has the highest melting point, although the heat of reaction with water is high. It is not sufficient enough to melt the metal and hence the reaction proceeds gently. Sodium has low melting point as compared to lithium, as it reacts with water, the heat of reaction is sufficient to melt it or even vapourise it. The molten metal thus spreads out, exposing a larger surface to water. As a result, Na reacts faster, gets hotter and catches fire. In case of K, Rb and Cs, they still have lower melting points and thus react explosively with water.

4.5.3 Reactivity Towards Dihydrogen

All the alkali metals react with dihydrogen at ~673 K (lithium reacts at 1073 K) to form colourless, crystalline ionic hydrides, $M^{\oplus}H^{\ominus}$.

$$2M + H_2 \xrightarrow{\Delta} 2MH \quad (M = Li, Na, K, Rb \text{ or } Cs)$$

4.5.3.1 Properties of Hydrides

1. Alkali metal hydrides have sodium chloride type structure.
2. These are salt-like compounds which are ionic in character ($M^{\oplus}H^{\ominus}$). These hydrides contain $H^{\ominus}$ ion (which is not

commonly found). It has been experimentally proved by the electrolysis of fused LiH that hydrogen is the negative component, as hydrogen is liberated at anode. Other hydrides decompose to metal and hydrogen before their melting points are reached.

3. The ionic character of the hydrides, MH, increases on moving from LiH to CsH.

   This can be explained on the basis of Fajans' rule. On moving from $Li^{\oplus}$ to $Cs^{\oplus}$, the size of the metal ion increases and its tendency to polarise the electron cloud of the anion ($H^{\ominus}$) decreases. Hence, the covalent character decreases or the ionic character increases.

   Ionic character: LiH < NaH < KH < RbH < CsH

4. The stability of the hydrides decreases from Li to Cs. Down the group (↓) from Li to Cs, the size of the alkali metal increases and hence the M–H bond becomes weaker and their stability decreases.

   Stability of the hydride: LiH > NaH > KH > RbH > CsH

5. The reactivity of the hydrides increases from Li to Cs.

   This is due to the decrease in the lattice energy of these hydrides as the size of the cation increases $[U \propto 1/(r_{\oplus} + r_{\ominus})]$ and thus the reactivity increases or stability decreases.

   Alkali metal hydrides react with protonic solvents (proton donor solvents such as water, alcohol, ammonia etc.) to liberate hydrogen (H_2).

   $$NaH + H_2O \longrightarrow \underset{\text{Sodium hydroxide}}{NaOH} + H_2\uparrow$$

   $$NaH + ROH \longrightarrow \underset{\text{Sodium alkoxide}}{RONa} + H_2\uparrow$$

   $$NaH + NH_3 \longrightarrow \underset{\text{Sodium amide}}{NaNH_2} + H_2\uparrow$$

   $$NaH + HC \equiv CH \longrightarrow \underset{\text{Sodium acetylide}}{NaC \equiv CNa} + 2H_2\uparrow$$

   Alkali metal hydrides are strong reducing agents. Their reducing character increases as their stability decreases. This behaviour is illustrated by reaction with oxygen. LiH is comparatively stable in dry air and reacts with oxygen only above red heat, sodium hydride inflames in oxygen, at 230°C, KH is inflamed in oxygen even at room temperature.

   $$NaH + O_2 \longrightarrow Na_2O + H_2O$$

4.5.4 Reactivity Towards Halogens

Alkali metals react vigorously with halogens forming halides of the type $M^{\oplus}X^{\ominus}$, an ionic crystalline solid (where M stands for alkali metal and X for halogen).

$$2M + X_2 \longrightarrow 2M^{\oplus}X^{\ominus}$$

(where M = Li, Na, K, Rb or Cs and X = F, Cl, Br or I)

The vigour of the reaction towards a particular halogen increases with an increasing atomic number of alkali metal, i.e. from Li to Cs, due to the decrease in the ionisation enthalpy of alkali metal. For example, rubidium reacts with chlorine more vigorously than sodium. On the other hand, reactivity of halogens towards a particular alkali metal decreases from F_2 to I_2, i.e. $F_2 > Cl_2 > Br_2 > I_2$.

Reactivity with particular halogen X_2		Reactivity with particular alkali metal M	
Li Na K Rb Cs	INCREASES	F_2 Cl_2 Br_2 I_2	DECREASES

4.5.5 Solubility in Liquid Ammonia

Alkali metals are highly soluble in liquid ammonia (solubility may be as high as 5 M).

Starting with pure ammonia:

1. As the concentration of alkali metal is increased, initially a light blue-coloured solution is obtained which exhibits the following behaviour:

   a. The density of the blue solution is less than that of liquid ammonia itself.

   b. The blue solution is considered as 'true solution'.

   c. Irrespective of the alkali metal, the colour of the solution is blue.

   d. Paramagnetic in nature.

   e. Good conductor of electricity.

   f. Strong reducing agent.

   Explanation: Solubility of alkali metal in liquid ammonia is due to the ionisation of alkali metal atom into ammoniated metal ion and ammoniated electron.

   $$M_{(s)} + (x+y)NH_3 \longrightarrow \underset{\text{Ammoniated metal ion}}{[M(NH_3)_x]^{\oplus}} + \underset{\text{Ammoniated electron}}{[e^-(NH_3)_y]^{\ominus}} \quad ...(4.1$$

   a. The electron, being very small and, therefore, strongly polarising, is able to orientate the solvent ammonia molecules round itself so that hydrogen points towards the electron. Essentially, the electron has made itself a cavity in the body of the solvent. The cavity model of solvation of electron (Fig. 4.4) suggests that the volume of the solution will increase due to the cavity created by the solvation of electrons and hence the density of the blue solution is less than that of ammonia itself.

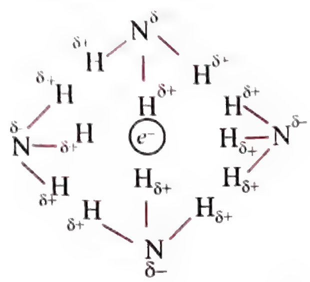


Fig. 4.4 Electron cavity model

b. The blue-coloured solution is a homogenous solution consisting of ammoniated metal ions and ammoniated electrons only, with particle size less than 10^{-9} m. Hence, it is considered as 'true solution'.

c. The blue colour of the dilute solution is due to ammoniated electrons which absorb energy corresponding to the red region of the visible light. The transmitted light or complimentary colour is blue, which imparts the blue colour to the solution.

This can be also explained in another way. The ammoniated electron absorbs photons in the visible light and exhibits an absorption band that has a maximum at ~15000 Å, which corresponds to blue colour. Since the colour of the solution is due to absorption by ammoniated electron, hence irrespective of the alkali metal dissolved in liquid ammonia, the colour of the solution remains same, i.e. blue.

d. The dilute solution contains a large number of unpaired or ammoniated electrons, and hence it is paramagnetic.

e. The solution is a good conductor of electricity due to the presence of ammoniated metal ions and ammoniated electrons.

f. The blue solution acts as a good reducing agent due to the presence of ammoniated electrons.

2. a. As the concentration of the alkali metal is between 1 M and 3 M, phase separation occurs, i.e. bronzecoloured solution floats on the blue solution formed previously.

b. As the concentration is greater than 3 M, the solution acquires bronze colour.

c. The bronze-coloured solution is diamagnetic.

Explanation: As the concentration of metal increases, solvated electrons undergo a pairing process.

$$[e^-(NH_3)_y]^{\ominus} + [e^-(NH_3)_y]^{\ominus} \rightleftharpoons [e^-_2(NH_3)_z]^{2-} \quad \ldots(4.2)$$

Also, the ammoniated metal ions and ammoniated electrons are appreciably associated to form aggregates.

$$[M(NH_3)_x]^{\oplus} + [e^-(NH_3)_y]^{\ominus} \rightleftharpoons [M(NH_3)_x]^{\oplus}\cdot[e^{\ominus}(NH_3)_y]^{\ominus} \quad \ldots(4.3)$$

$$[e^-_2(NH_3)_z]^{2-} + [M(NH_3)_x]^{\oplus} \rightleftharpoons [M(NH_3)_x]^{\oplus}\cdot[e^-_2(NH_3)_z]^{2-} \quad \ldots(4.4)$$

$$[e^-(NH_3)_y]^{\ominus} + [M(NH_3)_x]^{\oplus}[e^-(NH_3)_y]^{\ominus} \rightleftharpoons [e^-(NH_3)_y]^{\ominus}\cdot[M(NH_3)_x]^{\oplus}\cdot[e^-(NH_3)_y]^{\ominus} \quad \ldots(4.5)$$

$$[M(NH_3)_x]^{\oplus} + [M(NH_3)_x]^{\oplus}\cdot[e^-(NH_3)_y]^{\ominus} \rightleftharpoons [M(NH_3)_x]^{\oplus}\cdot[e^-(NH_3)_y]^{\ominus}\cdot[M(NH_3)_x]^{\oplus} \quad \ldots(4.6)$$

The product in Eq. (4.3) is a conventional non-conducting ion, although it is paramagnetic. Some of these higher aggregates are conducting and diamagnetic, as in Eqs. (4.2) and (4.5), and conducting and paramagnetic, as in Eqs. (4.4) and (4.6).

a. As the concentration of metal increases, the number of cavities increases. The cavities are maximum in bronze solution. This solution, therefore, has lower density than the blue solution and it floats on the blue solution.

b. As the concentration is greater than 3 M, the system contains less and less free solvent and it takes on the general characteristic of molten metal due to the formation of metal ion clusters, i.e. the colour of the solution changes to bronze and the solution acquires metallic lustre.

c. Due to the formation of electron clusters, in which ammoniated electrons with opposite spin group together [Eq. (4.2)], the bronze-coloured solution is diamagnetic.

3. The solution of alkali metal in liquid ammonia is unstable in the presence of impurities or catalysts (such as Fe), i.e. the blue colour fades away.

This is due to the formation of metal amide, along with the liberation of hydrogen.

$$2[M(NH_3)_x]^{\oplus} + 2[e^-(NH_3)_y]^{\ominus} \longrightarrow 2M(NH_2) + H_2\uparrow + (x+y-2)NH_3$$

or

$$2M + 2NH_3 \longrightarrow 2MNH_2 + H_2$$

However, under anhydrous conditions and in the absence of impurities and catalysts, this solution can be stored for many days.

4.5.6 Formation of Alums

Alums, $M^IM^{III}(SO_4)_2\cdot 12H_2O$, where M^I denotes alkali metal and M^{III} trivalent ion, represent one of the few cases where an alkali metal coordinates with six water molecules.

Lithium does not form alums because the lithium ion, $[Li(H_2O)_4]^{\oplus}$, is too small to be accommodated into the alum crystal.

4.5.7 Complex Formation in Alkali Metals

When a central metal atom or ion is bonded to a number of ligands [molecules/atoms/ions having donor atom(s)] by means of coordinate bond, the resulting species that is formed is known as *complex* or *coordination compound*. Complex formation can also be explained in terms of Lewis acid–Lewis base interaction.

M^{n+} $\longleftarrow$:	L
Lewis acid	Lewis base

(ion–dipole interaction)

Factors favouring complex formation are as follows:

1. Small size of the metal atom/ion
2. High charge
3. Presence of vacant *d*-orbitals of low energy for formation of bonds

The chemistry of metal ions in solution is essentially the chemistry of the complexes. As compared to other groups, alkali metals have very little tendency to form complexes. Because of the large size and single positive charge on the ion, the ion–dipole interaction between the potential ligands and the cations is weak, as in the hydrates.

Down the group (↓), the tendency to form complex decreases due to the increase in the size of the metal ion, charge-to-radius ratio, i.e. the charge density decreases and hence the ion–dipole interaction between the metal atom/ion and the ligand decreases down the group (↓).

Li > Na > K > Rb > Cs

4.6 GENERAL CHARACTERISTICS OF COMPOUNDS OF ALKALI METAL

4.6.1 OXIDES

When heated in excess oxygen, lithium forms monoxide (Li_2O), sodium forms peroxide (Na_2O_2) and potassium, rubidium and caesium form superoxide (MO_2, where M = K, Rb, Cs).

All the three types of oxides readily react with water to give hydroxides of the metals.

$$\underset{\text{Monoxide}}{M_2O} + H_2O \longrightarrow MOH \text{ (no } H_2O_2\text{; no } O_2)$$

$$\underset{\text{Peroxide}}{M_2O_2} + H_2O \longrightarrow MOH + H_2O_2 \text{ (no } O_2)$$

$$\underset{\text{Superoxide}}{MO_2} + H_2O \longrightarrow MOH + H_2O_2 + O_2$$

Statement: Whereas the reaction of alkali metal oxides with water is vigorous in case of Na, K, Rb and Cs, Li_2O is only slowly hydrolysed.

Explanation: This is due to the high lattice energy of Li_2O as compared to the monoxide of Na and others.

The peroxides and superoxides act as strong oxidising agents since they react with water to produce H_2O_2; H_2O_2 and O_2 respectively.

All the superoxides are yellow or orange-red in colour and are paramagnetic.

Superoxide ion has a three-electron bond $[:\ddot{O} \cdots \ddot{O}:]^{\ominus}$, i.e. it has one unpaired electron, which makes it coloured. Because of the presence of the unpaired electron, all superoxides are coloured and paramagnetic.

Configuration of superoxide ion ($O_2^{\ominus}$) on the basis of MOT:

$$\sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \sigma 2p_x^{\,2} \begin{bmatrix} \pi 2p_y^2 & \pi^* 2p_y^2 \\ \pi 2p_z^2 & \pi^* 2p_z^1 \end{bmatrix} \sigma^* 2p_x^0$$

All peroxides and monoxides are diamagnetic due to the absence of any unpaired electron or all the electrons are paired up.

Configuration of peroxide ion (O_2^{2-}) on the basis of MOT:

$$\sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \sigma 2p_x^{\,2} \begin{bmatrix} \pi 2p_y^2 & \pi^* 2p_y^2 \\ \pi 2p_z^2 & \pi^* 2p_z^2 \end{bmatrix} \sigma 2p_x^0$$

The monoxides and peroxides of higher elements are colourless, but those of the heavier elements are coloured. For example,

1. Monoxide of Li, Na, K is colourless but that of Rb_2O and Cs_2O is pale yellow and orange red, respectively. This is probably due to the presence of a small amount of superoxides RbO_2 and CsO_2, respectively.
2. Sodium peroxide is yellow in colour probably due to the presence of a small amount of sodium superoxide in it.

Reaction with ozone (O_3):

All alkali metals (except Li) form ozonides of the formula, MO_3

$$M_{(s)} + O_{3(g)} \longrightarrow \underset{\text{Alkali metal ozonide}}{MO_{3(s)}} \text{ (where M = Na, K, Rb, Cs)}$$

These ozonides are unstable and decompose on standing to form alkali metal superoxide and oxygen.

$$2MO_{3(s)} \longrightarrow \underset{\text{Alkali metal superoxide}}{2MO_{2(s)}} + O_{2(g)}$$

ILLUSTRATION 4.8

a. Monoxides of all alkali metals are hydrolysed by water, but lithium monoxide is slowly hydrolysed. Why?
b. Predict the product of the hydrolysis of KO_2.
c. Which of the following is paramagnetic: K_2O, K_2O_2, KO_2
d. Caesium oxide is expected to be strongly basic, weakly basic or acidic.

Sol.

a. Lithium monoxide is highly stable due to its high lattice energy (lattice energy $\propto 1/r_{\oplus} + r_{\ominus}$).
b. $2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$
c. KO_2 is paramagnetic, due to the presence of an unpaired electron in $O_2^{\ominus}$ (superoxide ion).
d. Caesium oxide is strongly basic.

ILLUSTRATION 4.9

Calculate the change in oxidation state of the oxygen, on reaction with the following alkali metals on heating: (a) Li, (b) Na and (c) Rb.

Sol.

a. $$Li + \underset{\text{(excess)}}{O_2} \xrightarrow{\Delta} \underset{\text{Lithium monoxide}}{Li_2O}$$

Let the oxidation state of O in $Li_2O = x$

Since the oxidation state of Li = +1

$\therefore\ 2(+1) + x = 0$

$x = -2$

The change in the oxidation state of oxygen is from 0 to −2.

b. $$Na_{(s)} + \underset{\text{(excess)}}{O_2} \xrightarrow{\Delta} Na_2O_{2(s)}$$

Let the oxidation state of 'O' in Na_2O_2 is x.

Since the oxidation state of Na is +1.

$\therefore\ 2(+1) + 2x = 0$

$x = -1$

The Change in oxidation state of oxygen is from 0 to −1.

c. $$Rb_{(s)} + \underset{\text{(excess)}}{O_2} \xrightarrow{\Delta} RbO_2(s)$$

Let the oxidation state of oxygen in RbO_2 is x.

Since the oxidation state of Rb is +1.

$\therefore\ (+1) + 2x = 0$

$x = -\frac{1}{2}$

The oxidation state of O in RbO_2 is −1/2. The change in oxidation state of O is from 0 to −1/2.

4.6.2 HYDROXIDES

Alkali metals form ionic hydroxides, MOH. They can be obtained by dissolving the metals or their oxides in water followed by evaporation of the solution.

$2M + 2H_2O \longrightarrow 2MOH + H_2\uparrow$

$M_2O + 2H_2O \longrightarrow 2MOH + H_2\uparrow$

But this method is not suitable for the preparation of the hydroxides of elements other than lithium because of the reaction being extremely vigorous (and explosive in some cases). The hydroxides are better prepared by electrolysis of the chlorides in aqueous solution.

The alkali metal hydroxides behave as strong bases. This is due to their low ionisation enthalpies. Due to the low ionisation enthalpy, the M–O bond is more polar as compared to the O–H bond and the M–O bond in MOH breaks easily to give $M^{\oplus}$ and $\overset{\ominus}{O}H$ ions.

$MOH \longrightarrow M^{\oplus} + \overset{\ominus}{O}H$

The strength of the base increases from LiOH to CsOH. The strength of the base depends upon the ease with which the hydroxide ion ($\overset{\ominus}{O}H$) can be separated from the metal ion. The separation of the $\overset{\ominus}{O}H$ from $M^{\oplus}$ ion depends on:

1. The polarity of the M–OH bond
2. The distance between M and OH in MOH

The greater the polarity of the bond, the greater is the ease of ionisation and hence greater the base strength. In case of alkali metal hydroxide, ionisation enthalpy of alkali metal decreases down the group and hence polarity of the M–OH bond increases.

Simultaneously, since the size of the alkali metal increases down the group (↓), the strength of the M–OH bond decreases.

As a result, M–OH can be more and more easily cleaved and hence the basic strength increases from LiOH to CsOH.

Basic strength: LiOH < NaOH < KOH < RbOH < CsOH

Solubility in water: LiOH is much less soluble in water than other hydroxides of the group due to its high lattice energy. The solubility of the hydroxides in water increases down the group (↓). Their concentrated solution is caustic or corrosive in nature. Hence, they are known as *caustic alkalis*.

Thermal stability: All the hydroxides are thermally stable, while LiOH is not. LiOH dissociates on heating to form Li_2O.

$LiOH \xrightarrow{\Delta} Li_2O + H_2O$

Since Li_2O is more stable as compared to LiOH (becasue of its high lattice energy), LiOH decomposes on heating.

Reaction with acids: Alkali metal hydroxides, being basic in nature, form salts on reaction with acids.

$KOH + HCl \longrightarrow KCl + H_2O$

$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$

The salts are colourless, ionic solids and are soluble in water.

4.6.3 HALIDES

The alkali metal halides MX (where M = Li, Na, K, Rb or Cs and X = F, Cl, Br or I) are all colourless, crystalline solids with high melting point. They can be prepared by the reaction of appropriate oxide, hydroxide or carbonate with aqueous hydrogen halide (HX).

$M_2O + 2HX \longrightarrow 2MX + H_2O$

$MOH + HX \longrightarrow MX + H_2O$

$M_2CO_3 + 2HX \longrightarrow 2MX + CO_2 + H_2O$

Halides of lithium crystallise from aqueous solution as hydrates, $LiX.3H_2O$ (where X = Cl, Br, I), whereas other alkali halides form anhydrous crystals. This is because of the high polarising ability of $Li^{\oplus}$ ion. It has the tendency to retain the solvent molecules as molecule of crystallisation, and crystallises from the aqueous solution as a hydrate, $LiX.3H_2O$.

All the halides have strong negative standard enthalpies of formation, but among the halides the $-\Delta_f H^{\ominus}$ values for fluorides decrease from lithium to caesium, the reverse is true for chlorides, bromides and iodides for a given element. $\Delta_f H^{\ominus}$ always becomes less negative as we go from fluoride to iodide (Table 4.5).

Table 4.5 Standard enthalpies of formation $\Delta_f H^{\ominus}$ of alkali metal halides

M	$-\Delta_f H^{\ominus}$ (MX)(kJ mol^{-1}) MF	MCl	MBr	MI
Li	612	409	350	271
Na	569	411	360	288
K	563	436	392	328
Rb	549	430	389	329
Cs	531	433	395	337

These trends can be interpreted in terms of the **Born–Haber cycle.** The reaction between metal and halogen resulting in the formation of metal halide can be theoretically broken down into a cycle of fundamental energy processes, such that the summation of the total energy in the cycle is equal to the enthalpy of formation of the halide.

Very high negative value of $\Delta_f H^{\ominus}$ for fluorides can be explained on the basis of the fact that the dissociation energy of fluorine molecule is the smallest and the lattice energy is the highest. Lattice energy is proportional to $1/r_0$ or $1/(r_{\oplus} + r_{\ominus})$. Hence, the lattice energy will be highest for LiF and lowest for CsI.

The variation in lattice energy is greatest when $r_{\ominus}$ is smallest and least when $r_{\ominus}$ is largest. Thus, the decrease in lattice energy of fluorides is very large on moving from lithium to caesium, whereas this decrease is smaller in case of chlorides, bromides and iodides. The heat of sublimation and ionisation enthalpy of the elements decrease from lithium to caesium. The sharp decrease in the lattice energy fluorides results in a decrease of $\Delta_f H^{\ominus}$ for fluorides. A small decrease in the lattice energy of chlorides, bromides and iodides does not force the $\Delta_f H^{\ominus}$

values of these halides to decrease from lithium to caesium. The unexpectedly larger negative values of $\Delta_f H^{\ominus}$ for potassium are due to its proportionately smaller values of sublimation and ionisation energy.

The trend in the values of melting point, boiling point and solubility can be explained in terms of polarisation effects, lattice energy and hydration enthalpy as discussed below:

1. **Polarisation effect:** When a cation, $M^{\oplus}$ of an ionic molecule $M^{\oplus}X^{\ominus}$ approaches closely the anion $A^{\ominus}$, it withdraws the electron cloud of the anion towards itself and thus the electron cloud of anion gets distorted from the symmetrical shape. This effect is called distortion or deformation or **polarisation** of anion $X^{\ominus}$ by the cation $M^{\oplus}$. The cation $M^{\oplus}$ is also deformed by the anion, $A^{\ominus}$. But due to the smaller size of the cation, the electron cloud is strongly held to the nucleus and hence the polarisation of the cation by the anion is negligible, and hence generally not considered.

The ability of a nearby cation to polarise a nearby anion is called its *polarising power* or *polarising ability* and the tendency of an anion to get polarised or distorted by a cation is called its *polarisability*. Factors affecting the magnitude of polarising power of as cation and polarisability of an anion as derived from Fajans' rules are given here.

a. **Charge on cation or anion:** The greater the charge on the cation greater is its polarising power and hence greater is the covalent character.

Example	$Na^{\oplus}Cl^{\ominus}$	$Be^{2+}Cl_2$	$Al^{3+}Cl_3$
Cation	$Na^{\oplus}$	Be^{2+}	Al^{3+}
Charge on cation	+1	+2	+3
Polarising power	$Na^{\oplus}$ <	Be^{2+} <	Al^{3+}
Covalent character	NaCl <	$BeCl_2$ <	$AlCl_3$

the greater the charge on the anion, more strongly it will be polarised by a cation, greater will be its polarisability.

Example	CH_4	NH_3	H_2O	HF
Anion	C^{4-}	N^{3-}	O^{2-}	$F^{\ominus}$
Charge on anion	–4 >	–3 >	–2 >	–1
Polarisability of anion	C^{4-} >	N^{3-} >	O^{2-} >	$F^{\ominus}$
Covalent character	CH_4 >	NH_3 >	H_2O >	HF

b. **Size of the cation:** The smaller is the size of the cation, greater is its polarising power to polarise nearby anion and hence greater is the covalent character.

Example	LiCl	NaCl	KCl	RbCl	CsCl
Size of cation	$Li^{\oplus}$ <	$Na^{\oplus}$ <	$K^{\oplus}$ <	$Rb^{\oplus}$ <	$Cs^{\oplus}$
Polarising power	$Li^{\oplus}$ >	$Na^{\oplus}$ >	$K^{\oplus}$ >	$Rb^{\oplus}$ >	$Cs^{\oplus}$
Covalent character	LiCl >	NaCl >	KCl >	RbCl >	CsCl

Thus covalent character decreases down the group.

c. **Size of the anion:** The larger the anion, greater is its polarisability and hence greater is the covalent character.

Example	NaF	NaCl	NaBr	NaI
Size of anion	$F^{\ominus}$ <	$Cl^{\ominus}$ <	$Br^{\ominus}$ <	$I^{\ominus}$
Polarisability of anion	$F^{\ominus}$ <	$Cl^{\ominus}$ <	$Br^{\ominus}$ <	$I^{\ominus}$
Covalent character	NaF <	NaCl <	NaBr <	NaI

d. **Electronic configuration of the cation:** If two different cations have the same size and charge, e.g. $Cu^{\oplus}$ (0.96 Å Charge = + 1) and $Na^{\oplus}$ (0.95 Å, Charge = + 1), then the cation having pseudo noble gas configuration or 18 electron valence shell configuration ($ns^2np^6nd^{10}$ configuration) has greater polarising power than cation with noble gas, i.e. 8 electron configuration (ns^2np^6 configuration).

This is because of the fact that the *d*-electrons of 18 electron shell shield the nuclear charge of the cation less effectively than the 8 electron shell. Hence, CuCl is more covalent than NaCl.

2. **Lattice enthalpy:** The greater the lattice enthalpy, greater will be the melting point of the alkali metal halide and lower will be its solubility in water as shown in Table 4.6.

Table 4.6 Lattice enthalpy, hydration enthalpy, melting point and solubility of some metal halide

Compound	LiCl	NaCl	KCl	RbCl	CsCl
Lattice enthalpy ($kJ\ mol^{-1}$)	–845	–770	–703	–674	–644
Hydration enthalpy ($kJ\ mol^{-1}$)	–876	–776	–700	–680	–646
Melting point (K)	887	1084	1039	988	925
Solubility (gL^{-1})	63.7	35.7	34.7	7.70	6.2

3. **Hydration enthalpy:** Higher the hydration enthalpy of the ions, greater is the solubility in water.

Hydration enthalpy depends on the charge density. Greater is degree of hydration, the greater is the hydration enthalpy since the size of ions increases from $Li^{\oplus}$ ion to $Cs^{\oplus}$ ion, the degree of hydration decreases from $Li^{\oplus}$ ion to $Cs^{\oplus}$ ion, i.e. $Li^{\oplus}$ ion is the heaviest hydrated and $Cs^{\oplus}$ ion is the least hydrated. As a result, the size of hydrated ions decreases from $Li^{\oplus}$ ion to $Cs^{\oplus}$ ion, and as a consequence ionic mobility increases from hydrated $Li^{\oplus}$ ion to hydrated $Cs^{\oplus}$ ion.

4. **Melting points and solubility:** Considering the above three factors, the melting points and solubility of alkali metal halides are explained as below.

Statement (i): For the same alkali metal, the melting point decreases in the order: Fluoride > Chloride > Bromide > Iodide.

Explanation: Keeping the alkali metal ion the same, the lattice energy of alkali metal halide decreases as the size of the halide ion increases $\left(U \propto 1/_{r_M \oplus + r_x \ominus}\right)$. As the lattice energy decreases,

the energy required to break the lattice decreases, i.e. melting point decreases.

Halides	NaF	NaCl	NaBr	NaI
Lattice energy ($kJ\ mol^{-1}$)	–919	–776	–745	–685
Melting point (K)	1261	1084	1028	994

Statement (ii): For the same halide ion, lithium halide has lower melting point than sodium halide and thereafter, the melting point decreases from sodium halide to caesium halide.

Order of M.Pt: NaX > KX > RbX > CsX > LiX

Explanation: Lithium halide is covalent whereas sodium halide is ionic because of high polarising ability of small size $Li^{\oplus}$ ion as compared to $Na^{\oplus}$ ion. Because of the covalent nature of lithium halide it has lower melting point as compared to sodium halide. Thereafter, the melting point decreases from sodium halide to caesium halide due to decrease in lattice energy with the increases in the size of alkali metal ion.

Halides	LiCl	NaCl	KCl	RbCl	CsCl
Melting point (K)	887	1084	1039	988	925

Statement (iii): The solubility of most of the alkali metal halides except those of fluorides decreases down the group(↓).

Explanation: For a compound to be soluble, solvation energy (hydration energy) should be greater than the lattice energy of the compound. Down the group (↓), since the decrease in hydration enthalpy is more than the decrease in lattice enthalpy, solubility decreases.

Statement (iv): Lithium halides are soluble in organic solvents such as alcohol, acetone etc. whereas sodium halides are insoluble in organic solvents.

Explanation: Because of the small size and high electronegativity, lithium halides are predominantly covalent and hence are soluble in organic solvents. Sodium halides being ionic are insoluble in organic solvents.

Statement (v): LiF is sparingly soluble in water. However, on moving down the group (↓), the solubility of alkali metal fluorides increases.

Solubility in water: LiF < NaF < KF < RbF < CsF

Explanation: Due to the high hydration enthalpy of $Li^{\oplus}$ ion, lithium halides are soluble in water, except LiF which is sparingly soluble in water due to its high lattice enthalpy. However, on moving down the group (↓) from NaF to CsF, solubility increases, as the decrease in the lattice enthalpy more than compensates the decrease in the hydration enthalpy.

4.6.4 Nitrides

Only Lithium combines directly with nitrogen (N_2) to form nitride, Li_3N which is ionic solid.

Despite the fact that lithium having the highest ionisation energy of all the alkali metals is most reactive towards nitrogen.

This can be explained on the basis of the fact that the lattice energy of the compound formed from small cation and small anion is the highest. Since N^{3-} (nitride ion) is a small anion and hence the lattice energy of the compound formed with the small cation $Li^{\oplus}$ is the high heat and hence high heat of formation or Li_3N is the most stable nitride among the alkali metal nitride.

$$\text{Lattice energy} \propto \frac{1}{r^{\oplus} + r^{'}}$$

$$6Li_{(s)} + N_2 \longrightarrow 2Li_3N_{(s)}$$

Li_3N is rapidly hydrolysed by water, thus liberating ammonia, NH_3.

$$Li_3N + 3H_2O \longrightarrow 2LiOH + NH_3$$

The nitrides of other alkali metals can be made by indirect methods. Sodium nitride (Na_3N) can be made by dissolving sodium and sodium azide (NaN_3) in liquid ammonia, allowing ammonia to evaporate and then warming the mixture.

$$NaN_3 + Na \longrightarrow 3NaOH + NH_3$$

It decomposes with the loss of nitrogen above 150°C. It is readily hydrolysed.

$$Na_3N + 3H_2O \longrightarrow 3NaOH + NH_3$$

4.6.5 Carbides

Only lithium reacts with carbon to form an ionic carbide, Li_2C_2. This is because of high lattice energy of lithium carbide, Li_2C_2 being made up of small cation ($Li^{\oplus}$) and small anion (C_2^{2-}).

Other alkali metals form similar carbides when heated with acetylene or when acetylene is passed through a solution of the metal in liquid ammonia.

$$\underset{\text{or } C_2H_2}{Na + HC \equiv CH} \rightarrow \underset{\text{or } Na_2C_2}{\overset{\oplus}{Na}\,\overset{\ominus}{C} \equiv \overset{\ominus}{C}\,\overset{\oplus}{Na}}$$

These compounds react with water to give acetylene and contain $(C \equiv C)^{2-}$ ion, hence they are termed acetylides.

$$\underset{\text{or } Na_2C_2}{\overset{\oplus}{Na}\,\overset{\ominus}{C} \equiv \overset{\ominus}{C}\,\overset{\oplus}{Na}} + H_2O \rightarrow 2NaOH + \underset{\text{or } C_2H_2}{HC \equiv CH}$$

The heavier alkali metals, i.e. potassium, rubidium and caesium form interstitial carbides when heated with graphite, the graphite lattice expanding to accommodate the metal atoms between the layers of carbon atoms. The compounds formed are non-stoichiometric and highly coloured, the colour varies with variable composition.

$$\underset{\text{Dark grey}}{C_{60}K} \xrightarrow{+K} \underset{\text{Blue}}{C_{36}K} \xrightarrow{+K} C_{24}K + C_8K \text{ (Bronze)}$$

4.6.6 Sulphides

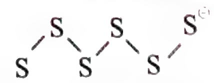
Alkali metals react with sulphur to form sulphides of formulae M_2S_x, where $x = 1, 2, 3, 4, 5$ or 6.

Monosulphides are prepared by burning metals in sulphur vapour or by high temperature reduction of their sulphates with carbon. e.g.

$$2Na + S \longrightarrow Na_2S$$

$$Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO$$

Polysulphides are formed by the action of sulphur on metal solution in liquid ammonia. The polysulphide ions are present in the crystal lattice as the zig-zag chain of sulphur atoms.



Solution of the alkali metal sulphides are strongly alkaline due to the hydrolysis of the sulphide ion.

$$S^{2-} + H_2O \longrightarrow HS^{\ominus} + OH^{\ominus}$$

$$HS^{\ominus} + H_2O \longrightarrow H_2S + OH^{\ominus}$$

As compared to monosulphides, polysulphides are much less readily hydrolysed because the negative charge is distributed over all the sulphur atoms instead of being concentrated on one. This makes the anion a poorer electron donor.

The sulphides behave as reducing agents being oxidised to sulphur or its oxides; and are easily oxidised by even weak oxidising agents.

4.6.7 Oxocompounds or Salts of Oxoacids

As alkali metals are highly electropositive, their hydroxides are strong bases and hence they react with all oxoacids to form corresponding salts. Oxoacids are those in which the acidic proton is on hydroxyl group with the oxo group attached to the same atom, e.g. carbonic acid (H_2CO_3), nitric acid (HNO_3), sulphuric acid (H_2SO_4) etc. They are generally soluble in water and thermally stable.

4.6.7.1 Carbonates and Bicarbonates

Carbonates of the type M_2CO_3 are known for all the alkali metals. Lithium carbonate (Li_2CO_3) being the least soluble in water is prepared by adding a solution of sodium carbonate in an aqueous solution of lithium chloride, when Li_2CO_3 precipitates out.

$$2LiCl + Na_2CO_3 \longrightarrow Li_2CO_3\downarrow + 2NaCl$$

Li_2CO_3 can also be prepared by passing CO_2 through a solution of LiOH.

$$2LiOH + CO_2 \longrightarrow Li_2CO_3 + H_2O$$

When CO_2 is passed through cold concentrated solutions of other alkali metal hydroxides, their carbonates are not precipitated because of their much greater solubilities in water. However, if these solutions are saturated with CO_2, their bicarbonates are precipitated as the bicarbonates are much less soluble than the corresponding carbonates. When these bicarbonates are heated strongly, they decompose to give carbonates.

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3\downarrow$$

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2\uparrow$$

Sodium carbonate (Na_2CO_3) is manufactured from brine. The brine is treated with a mixture of CO_2 and NH_3 when sodium bicarbonate ($NaHCO_3$) precipitates out. This bicarbonate when heated gives carbonates.

$$2\,NaCl + 2CO_2 + 2NH_3 + 2H_2O \longrightarrow \underset{\text{Less soluble}}{2\,NaHCO_3} + 2NH_4Cl$$

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

Potassuim carbonate (K_2CO_3) cannot be made by similar method since potassium bicarbonate is more soluble than sodium bicarbonate and it is not precipitated when an ammonical solution of KCl is saturated with carbon dioxide. KOH, therefore, is prepared from reaction of hydroxide and CO_2.

Lithium does not form a solid bicarbonate (due to its less electropositive nature), though it exists in solution because the bicarbonate is less soluble than the carbonate due to the smaller size of the lithium ion.

The reactivity of the alkali metal carbonates is very similar since these are almost entirely of the anion, CO_3^{2-}. Lithium carbonate varies slightly from the rest. As the electropositive character increases from Li to Cs, the stability of the carbonates and hydrogen carbonates increases in the same order.

$$Li_2CO_3 < Na_2CO_3 < K_2CO_3 < RbCO_3 < CsCO_3$$

$$LiHCO_3 < NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3$$

The thermal stabilities of the alkali metal carbonates w.r.t. its decomposition to their oxides and CO_2 increase with the increasing size of the cation.

$$M_2CO_3 \xrightarrow{\Delta} M_2O + CO_2\uparrow$$

The decomposition of carbonates and bicarbonates takes place because the oxides of alkali metals are more stable than their oxoacid salts. The relative ease of decomposition parallels the decrease in ionic radius of the cation from $Cs^{\oplus}$ to $Li^{\oplus}$, which in turn increases the lattice energy of the solid reaction products. The lattice energy of the carbonates of alkali metals varies from one another in smaller amounts as it mainly depends upon the larger anion, CO_3^{2-}. Moreover, the $Li^{\oplus}$ ion being smaller in size, polarises the large CO_3^{2-} ion giving a larger covalent character to the carbonate. The difference in the lattice energy of carbonates and oxides of alkali metals decreases on moving from lithium to caesium, hence lesser is the tendency of the carbonates to decompose to oxide.

The aqueous solution of carbonates are alkaline. This is due to the hydrolysis as carbonates are salts of strong bases and weak acid (H_2CO_3, carbonic acid).

$$M_2CO_3 + 2H_2O \rightleftharpoons \underset{\substack{\text{Strong}\\ \text{alkali}}}{2MOH} + \underset{\substack{\text{Carbonic}\\ \text{acid}}}{H_2CO_3}$$

4.6.7.2 Nitrates

Alkali metals form nitrates of the type, MNO_3.

1. These are colourless, soluble in water and electrovalent in nature.
2. Nitrates of lithium and sodium are deliquescent in nature in the solid state.
3. On heating, all the alkali metal nitrates, except lithium nitrates, decompose to give nitrites.

$$2MNO_3 \xrightarrow{\Delta} 2MNO_2 + O_2 \text{ (where M = Na, K, Rb, Cs)}$$

Lithium nitrate decomposes to give monoxide.

$$2LiNO_3 \xrightarrow{\Delta} Li_2O + 2NO_2 + \frac{1}{2}O_2$$

This is attributed to lower thermal stability of lithium nitrite, $LiNO_2$. The size of the $NO_2^{\ominus}$ ion is large enough to be deformed by the small $Li^{\oplus}$ ion to make it much less stable than Li_2O.

4.7 ANOMALOUS BEHAVIOUR OF LITHIUM

The elements in the second period have $1s^2$ as their inner core. These elements exhibit certain properties which are different from the rest of the members of their respective groups. Many of the properties of Li (the first member of group I, i.e. alkali metals) are different from the rest of the elements of group I.

The main reasons for anomalous behaviour of Li can be attributed to:

1. Extremely small size of the Li atom and the $Li^{\oplus}$ ion.
2. High polarising power $\left(\text{i.e. } \dfrac{\text{ionic charge}}{(\text{ionic radius})^2}\right)$ of the $Li^{\oplus}$ ion, which leads to its increased tendency for covalent bond formation. Its compounds are therefore soluble in organic solvents.
3. Least electropositive character and highest IE as compared to other alkali metals.
4. Absence of *d*-orbitals in valence shell of Li.

Points of difference between lithium and other alkali metals:

1. Lithium is harder and lighter as compared to other alkali metals.
2. Its melting and boiling points are much higher than the rest of alkali metals.
3. Due to its small size, it forms stable compounds with small anions such as hydride, carbide, nitride.

   $$6Li + 3N_2 \longrightarrow \underset{\text{Lithium nitride}}{2Li_3N}$$

   $$2Li + 2C \xrightarrow{\Delta} \underset{\text{Lithium carbide}}{Li_2C_2}$$

   The reactions between lithium and hydrogen, carbon or nitrogen are exothermic.
4. Lithium, unlike other alkali metals, forms no acetylide on reaction with ethyne.

   $$Li + C_2H_2 \longrightarrow \text{No reaction}$$

   $$2Na + C_2H_2 \longrightarrow \underset{\text{Disodium acetylide}}{Na_2C_2} + H_2$$
5. Lithium, on reaction with oxygen, forms only monoxide (Li_2O) whereas other alkali metals form peroxides (M_2O_2) and superoxide (MO_2).
6. Lithium reacts very slowly with water whereas the reactions of other alkali metals are violent.
7. LiOH is a weaker base and sparingly soluble in water as compared to other alkali metal hydroxides.
8. LiOH decomposes at red heat to Li_2O, whereas other alkali metal hydroxides sublime unchanged as MOH.

   $$2LiOH \longrightarrow Li_2O + H_2O$$
9. Lithium halides are deliquescent and crystallises as a hydrate $LiCl.2H_2O$, whereas other alkali metals do not form hydrates.
10. Lithium halides are covalent and dissolve in organic solvents like alcohol, pyridine etc.
11. Lithium bicarbonate is not obtained in the solid form (exists in solution) while all the other alkali metals form solid bicarbonates.
12. Lithium carbonate decomposes to lithium oxide on heating, whereas carbonates of other alkali metals are more stable to heat.

    $$Li_2CO_3 \longrightarrow Li_2O + CO_2\uparrow$$
13. Lithium nitrate, on heating, decomposes to lithium oxide, Li_2O, whereas the nitrates of other alkali metals give nitrites.

    $$4\,LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

    $$2\,NaNO_3 \xrightarrow{\Delta} 2\,NaNO_2 + O_2$$
14. Li_2SO_4 does not form an alum, whereas the sulphates of other alkali metals do so.
15. Alkyl and aryls of lithium are more stable.
16. Lithium shows a greater tendency to form complexes.

4.8 DIAGONAL RELATIONSHIP OF LITHIUM WITH MAGNESIUM

The elements of the second period of periodic table resemble the elements at their lower right in the third period (i.e. diagonally placed element) more than the members of their respective group. This is known as diagonal relationship.

Lithium resembles its diagonally opposite element magnesium mainly because of nearly the same charge density (charge/size ratio):

1. Atomic radii of Li are 152 pm, whereas that of magnesium are 160 pm.
2. Ionic radii of $Li^{\oplus}$ are 76 pm, whereas that of Mg^{2+} are 72 pm.

Main points of similarity are as follows:

a. Lithium has high melting and boiling points, which are comparable with those of magnesium.

b. Lithium is as hard as magnesium.

c. On reaction with oxygen, lithium forms monoxide (Li_2O), similarly magnesium also forms monoxide (MgO).

$$4\,Li + O_2 \longrightarrow 2Li_2O$$

$$2Mg + O_2 \longrightarrow MgO$$

d. Unlike other alkali metals, Lithium reacts directly with carbon forming carbide, magnesium also forms carbide.

e. Like magnesium, lithium forms nitride when heated with nitrogen. Other alkali metals do not do so.

$$6Li + N_2 \xrightarrow{\Delta} 2Li_3N$$

$$3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$$

f. The hydroxides, carbonates and nitrates of lithium as well as of magnesium decompose on heating to give oxides.

$$LiOH \xrightarrow{\Delta} Li_2O + H_2O$$

$$Mg(OH)_2 \xrightarrow{\Delta} MgO + H_2O$$

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$$

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

$$2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$$

g. Lithium hydroxide (LiOH) is less soluble, less basic and decomposes on heating to Li_2O. The hydroxides of other alkali metals are strongly basic, highly soluble and sublime as MOH on strong heating. Magnesium hydroxide, $Mg(OH)_2$, is also sparingly soluble, less basic and decomposes on heating to MgO.

h. Both lithium and magnesium nitrates, on heating decompose to give their oxides.

$$4\,LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

$$2\,Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$$

i. Li_2CO_3, LiOH, LiF and Li_3PO_4 are the only alkali metal salts which are sparingly soluble in water, similar to the corresponding magnesium compounds.

j. The compounds of lithium have a covalent character similar to those of magnesium. Both LiCl and $MgCl_2$ are soluble in organic solvents, e.g. alcohol.

k. The compounds of lithium are heavily hydrated similar to those of magnesium. $LiCl{\cdot}2H_2O$, $MgCl_2{\cdot}6H_2O$

l. Both LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates, $LiCl{\cdot}2H_2O$ and $MgCl_2{\cdot}6H_2O$.

m. Both lithium and magnesium do not form solid bicarbonates (exist in solution state).

n. Both lithium perchlorate ($LiClO_4$) and magnesium perchlorate [$Mg(ClO_4)_2$] are highly souble in ethanol.

4.9 ALKALI METALS: EXTRACTION AND USES

The extraction of alkali metals cannot be carried out by usual procedures due to the following:

1. Alkali metals cannot be extracted by reduction of their oxides as they themselves are the strongest reducing agent and hence no other metal can displace them from their oxides.
2. The alkali metals are highly reactive towards water, therefore the method of displacing them from their solutions by using elements high in the electrochemical series is not possible.
3. These elements can be prepared by electrolysis of their aqueous solutions using mercury cathode only wherein they form amalgams but the recovery of the metal from the amalgam is very difficult. Moreover, during electrolysis of aqueous solutions the liberated metal at the cathode reacts with water to form metal hydroxide.

Keeping in view the above difficulties, alkali metals are usually isolated by the electrolysis of their fused metal halides along with another metal halide (to lower the melting point).

4.9.1 EXTRACTION

Lithium: The important minerals of lithium include spodumene, $LiAlSi_2O_6$; lepidolite, $Li_2Al_2(SiO_3)_3(F{\cdot}OH)_2$ and amblygonite, $LiAl(PO_4)F$. The extraction of lithium involves two steps:

1. **Preparation of lithium chloride from the minerals:** The ore is first heated to about 1373 K to convert it into more friable form, which is then washed with sulphuric acid at 523 K and is leached with water to give lithium sulphate, $Li_2SO_4{\cdot}H_2O$. Successive treatment with sodium carbonate and hydrochloric acid gives first Li_2CO_3 and finally lithium chloride, LiCl. Alternatively, lithium chloride can be obtained by calcining the washed ore with $CaCO_3$ at 1273 K followed by leaching with water to give LiOH and then treatment with HCl.
2. **Electrolysis of lithium chloride:** The electrolyte consists of a fused mixture of 55% LiCl and 45% KCl at 723 K. On electrolysis, the molten lithium containing about 1% potassium is collected (Fig. 4.5).

   Alternatively, electrolysis of LiCl solution in pyridine, ethanol or acetone can be done.

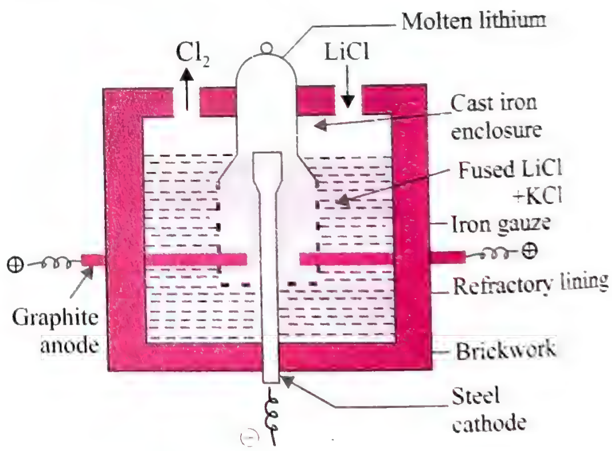


Fig. 4.5 Electrolysis of lithium chloride

Sodium: Enormous quantities of sodium chloride occur as rock-salt deposits and in sea water. Other compounds of sodium found in nature include sodium carbonate, Na_2CO_3, double sulphate with Ca, borate as borax and complex silicates.

Sodium is extracted by electrolysis of a fused mixture of sodium chloride (40%) and calcium chloride (60%) at 1123 K, in Downs cell. Metallic sodium and calcium are liberated at the cylindrical steel cathode and rise through a cooled collecting pipe which allows calcium to solidify and fall back into the melt. Molten sodium is taken out of the cell (Fig 4.6).

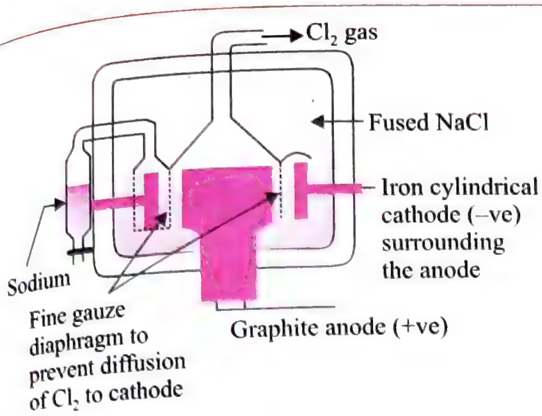


Fig. 4.6 Downs cell

The function of calcium chloride is to lower the operating temperature from 1080 K (m.pt. of NaCl) to about 850 K. The main reasons for lowering the temperature are as follows:

1. The melting point of sodium choride is very high and it is very difficult to maintain it in the molten state during electrolysis.
2. Sodium is considerably volatile at the temperature needed for the electrolysis and therefore, a part of the metal produced vapourises.
3. Molten sodium gets dispersed in molten sodium chloride to form a metallic fog at a high temperature.
4. Both sodium and chlorine, the two products of the electrolysis, have a corrosive action on the material of the vessel employed for the electrolysis at such a high temperature.

Potassium: Potassium is obtained by electrolysis of fused potassium hydroxide (KOH)

$$KOH \rightleftharpoons K^{\oplus} + \overset{\ominus}{O}H$$

At cathode: $K^{\oplus} + e^- \longrightarrow K$

At anode: $4\,\overset{\ominus}{O}H \longrightarrow O_2 + 2H_2O + 4e^{\ominus}$.

Potassium can also be obtained by reduction of KCl with sodium vapours at about 1125 K in large fractionating tower.

$$KCl + Na \longrightarrow NaCl + K$$

Potassium obtained by this method is about 99.5% pure.

4.9.2 Uses of Alkali Metals and their Compounds

Lithium:

1. It is used in making alloys:
   a. Lithium–magnesium alloy (with 14% Li): Addition of lithium to magnesium improves its tensile strength and makes its resistant to corrosion. It is used for making armour plate and aerospace components.
   b. Lead–lithium alloy or white metal is used for making toughened bearings and sheaths of electric cables.
   c. Lithium–aluminum alloy: It is used for aircraft construction because of its high strength.
2. As deoxidiser: It is used as a deoxidiser in the purification of nickel and copper.
3. In the manufacture of glass and pottery: Lithium carbonate is used to increase the strength and resistance of glass. Lithium salts are used in ceramics to prevent surface cracking of pottery.
4. As lubricants: LiOH is used in the manufacture of high quality lubricating greases, which can withstand extreme variation of temperature.
5. In medicine: Lithium bromide is used as a sedative.
6. Lithium hydride is used as a source of hydrogen for meteorological purposes and for filling of balloons.
7. As scavanger: Since it readily combines with oxygen and nitrogen, thus it is used for removing the last traces of oxygen and nitrogen during refining of metals such as copper and nickel.

Sodium:

1. As a reducing agent in the form of sodium amalgam .
2. As a reagent in organic chemistry—Used in Lassaigne's test for the detection of extra elements (nitrogen, sulphur and halogens) in organic compounds.
3. Molten (liquid) sodium or its alloy with potassium is used as a coolant in nuclear reactors.
4. Sodium can be used alone or with potassium to dry solvents.
5. Sodium is used for refining of metals such as zirconium and potassium.
6. Sodium is used in sodium vapour lamp.
7. Because of its lightness and high thermal conductivity, it is used to fill exhaust valves of aeroplanes engines.
8. Sodium–lead alloy is used for the preparation of tetraethyl lead, $Pb(C_2H_5)_4$, which is used as an antiknock agent in petrol.

$$\underset{\text{Lead–sodium alloy}}{(Pb + 4Na)} + 4C_2H_5Cl \longrightarrow \underset{\text{Tetraethyl lead}}{(C_2H_5)_4Pb} + 4NaCl$$

9. Sodium and sodium amalgam are used as reducing agents in organic synthesis.
10. It is used in the preparation of useful regents as NaCN, Na_2O_2 and $NaNH_2$.

Potassium:

1. Potassium forms an alloy with sodium, known as NaK (or 'nack') which is used as dessicant to produce dry solvents. It is also used as a medium for heat transfer in several industries.
2. Potassium vapour is used in different variety of magnetometers.
3. Potassium chromate is used in manufacturing ink, dyes, safety matches, fireworks, fly paper etc. It is also needed in the tanning of leather.
4. Potassium nitrate is used as a fertiliser.

Rubidium:

1. Rubidium is used in photocells.
2. It is used as a getter (remover of gases) in vacuum tubes.
3. Rubidium-87 is slightly radioactive and has been used extensively in dating rocks.

4. Rubidium salts are used in glasses and ceramics.
5. Rubidium compounds give a purple colour in fireworks.

Caesium:

1. Used in photoelectric cells and vacuum tubes.
2. It is used as a getter (remover of gases) in electron tubes.
3. Used as a catalyst in the hydrogenation of few organic compounds.
4. It is used in alarm clocks (Cs-133).

ILLUSTRATION 4.10

a. Which alkali metal is used as a coolent in nuclear reactor?
b. What is the oxidation state of K in KO_2?
c. The $E^{\ominus}$ for $Cl_2/Cl^{\ominus}$ is +1.36, for $I_2/I^{\ominus}$ is +0.53, for $Ag^{\oplus}/Ag$ is + 0.79, for $Na^{\oplus}/Na$ is –2.71 and for $Li^{\oplus}/Li$ is –3.04.
Arrange the following ionic species in decreasing order of reducing strength.
$I^{\ominus}$, Ag, $Cl^{\ominus}$, Li, Na
d. Why is KO_2 is paramagnetic?

Sol.

a. Sodium
b. The superoxide species is represented as $O_2^{\ominus}$. Since the compound is neutral, therefore the oxidation state of potassium is +1.
c. The order is $Li > Na > I^{\ominus} > Ag > Cl^{\ominus}$.
d. The superoxide $O_2^{\ominus}$ is paramagnetic, because of one unpaired electron in π^*2p antibonding molecular orbital.

ILLUSTRATION 4.11

Give reason for the following:
a. Why potassium is less reactive than rubidium?
b. Irrespective of the alkali metal dissolved in liquid ammonia, dil solution is always blue coloured.

Sol.

a. The atomic size of potassium is smaller as compared to rubidium, thus the valence shell electron (ns^1) is more loosely bound in rubidium. As a result, ionisation enthalpy of potassium is more than rubidium and hence potassium is less reactive than rubidium.
b. Alkali metals dissolve in liquid ammonia to give ammoniated metal ion and ammoniated electron.

$$M_{(s)} + (x+y)\,NH_3 \longrightarrow \underset{\text{Ammoniated metal ion}}{[M(NH_3)_x]^{\oplus}} + \underset{\text{Ammoniated electron}}{[e(NH_3)_y]^{\ominus}}$$

The blue colour is because of ammoniated electron which absorbs energy corresponding to the red region of the visible light and gives complimentary blue colour.

ILLUSTRATION 4.12

Sodium fire in the laboratory should not be extinguished by using water. Why?

Sol. Sodium reacts violently with water

$$Na + H_2O \longrightarrow NaOH + H_2\uparrow$$

thus producing sodium hydroxide and hydrogen gas. As H_2 gas is inflammable, it catches fire. As a result, the fire spreads. Therefore, water should not be used to extinguish the fire caused by sodium (instead CCl_4 should be used).

ILLUSTRATION 4.13

Choose the correct answers:

a. Which of the following alkali metal is the most electropositive?
i. Na ii. K iii. Rb iv. Cs
b. Which of the following alkali metals has the lowest m.pt.?
i. Li ii. K iii. Na iv. Rb
c. Which of the following is the strongest reducing agent?
i. Li ii. Na iii. K iv. Rb

Sol.

a. (iv) Cs, because of its low IE values.
b. (iv) Rb, metallic bending is weakest in Rb.
c. (i) Li.

ILLUSTRATION 4.14

LiH, LiF and Li_3N show exceptional thermal stabilities. Comment.

Sol. $Li^{\oplus}$ ion has very small size and has an exceptionally high charge to radius ratio and therefore salts of $Li^{\oplus}$ ion with small anions viz. $H^{\ominus}$, $F^{\ominus}$ and N^{3-} are highly stable due to their high lattice energy.

$$U \propto \frac{1}{r^{\oplus} + r_{\ominus}}$$

Thus LiH, LiF and Li_3N show exceptionally high thermal stability.

ILLUSTRATION 4.15

Salt of $Li^{\oplus}$ with large anions CO_3^{2-}, $NO_3^{\ominus}$ are relatively less stable than its salts with small anions. Comment.

Sol. Stability of a compound can be explained on the basis of its lattice energy ($\Delta_U H^{\ominus}$) which is inversely proportional to the sum total of the radius of cation and anion.

$$\text{Lattice energy} \propto \frac{1}{r_{\oplus} + r_{\ominus}}$$

Since $Li^{\oplus}$ ion is exceptionally small in size, it will form stable complexes with small size anions, due to high lattice energy of the compound formed, whereas compound of $Li^{\oplus}$ ion with large size anion CO_3^{2-} and $NO_3^{\ominus}$ are relatively less stable due to the less lattice energy.

ILLUSTRATION 4.16

Among LiF and LiI, which has more covalent character and why?

Sol. LiI has more covalent character. $F^{\ominus}$ ion is smaller in size as compared to $I^{\ominus}$. According to Fajans' rule, the large-sized anion $I^{\ominus}$ is polarised to a greater extent than small size anion, $F^{\ominus}$ ion. Greater polarisation of the anions leads to greater covalent character, i.e. LiI is more covalent as compared to LiF.

ILLUSTRATION 4.17

Among LiF and LiI, which is more soluble in water and why?

Sol. LiF is more soluble in water. According to Fajans' rule, $F^{\ominus}$ ion, being smaller as compared to $I^{\ominus}$ ion, will be polarised to a greater extent. Hence LiF will be less covalent as compared to LiI and hence LiF will be more soluble in water as compared to LiI.

ILLUSTRATION 4.18

Arrange the following in order of the increasing covalent character:

MCl, MBr, MF, MI (where M = alkali metals)

Sol.

	MF <	MCl <	MBr <	MI
Size of anion	$F^{\ominus}$ <	$Cl^{\ominus}$ <	$Br^{\ominus}$ <	$I^{\ominus}$
Degree of polarisation	$F^{\ominus}$ <	$Cl^{\ominus}$ <	$Br^{\ominus}$ <	$I^{\ominus}$
Covalent character	MF<	MCl <	MBr <	MI

With increasing size of the anion, degree of polarisation by the cation increases and hence the covalent character increases.

ILLUSTRATION 4.19

a. When is an ion highly polarising? Which alkali metal ion has the highest polarising power?

b. What makes lithium to show properties uncommon to the rest of the alkali metals?

Sol.

a. A cation is highly polarising if its (charge/radius) ratio is high. $Li^{\oplus}$ ion having the smallest size will have the maximum (charge/radius) ratio or polarising power.

b. Lithium shows properties uncommon to the rest of alkali metals due to:

i. Small size of Li atom and $Li^{\oplus}$ ion.

ii. High (charge/radius) ratio of $Li^{\oplus}$ ion.

4.10 SOME IMPORTANT COMPOUNDS OF SODIUM (Na)

4.10.1 Sodium Peroxide (Na_2O_2)

Common name: Oxone

Preparation: It is manufactured on industrial scale by heating sodium metal and moisture in excess of air (free from CO_2 and moisture) at 620 K.

$$\underset{}{2Na} + \underset{(air)}{O_2} \xrightarrow{620K} Na_2O_2$$

Properties:

1. When pure, it is colourless powder, but the faint yellow colour of the usual product arises due to the presence of a small amount of sodium superoxide NaO_2.
2. When Na_2O_2 comes in contact with mosit air, turns white due to the formation of Na_2CO_3.

$$2Na_2O_2 + 2H_2O \longrightarrow 4\,NaOH + O_2$$
$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

3. Sodium peroxide acts as a powerful oxidising agent that oxidises chromium (III) hydroxide to chromate, manganese (II) to manganate.

$$[O_2^{2-} + 2H_2O + 2e^{\ominus} \longrightarrow 4\overset{\ominus}{O}H] \times 3$$
$$[Cr(OH)_3 + 5\overset{\ominus}{O}H \longrightarrow CrO_4^{2-} + 4H_2O + 3e^-] \times 2$$
$$2Cr(OH)_3 + 3O_2^{2-} \longrightarrow 2CrO_4^{2-} + 2\overset{\ominus}{O}H + 2H_2O$$

$$[O_2^{2-} + 2H_2O + 2e^{\ominus} \longrightarrow 4\overset{\ominus}{O}H] \times 2$$
$$Mn(OH)_2 + 6\overset{\ominus}{O}H \longrightarrow MnO_4^{2-} + 4H_2O + 4e^-$$
$$Mn(OH)_2 + 2O_2^{2-} \longrightarrow MnO_4^{2-} + 2\overset{\ominus}{O}H$$

4. **Action of water:** When warm water is dropped over sodium peroxide, a steady stream of oxygen gas is produced at room temperature.

$$2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2\uparrow$$

5. **Action of acids:**
   a. On reaction with cold dilute H_2SO_4, gives hydrogen peroxide.

   $$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

   b. On reaction with hot acids, gives oxygen.

   $$2Na_2O_2 + H_2SO_4 \longrightarrow 2Na_2SO_4 + 2H_2O + O_2\uparrow$$

6. Na_2O_2 on reaction with absolute alcohol (at 273 K) gives a white powder of sodium hydrogen peroxide, NaOOH.

$$Na_2O_2 + C_2H_5OH \longrightarrow C_2H_5ONa + NaOOH$$

7. On reaction with carbon monoxide (CO), gives sodium carbonate.

$$Na_2O_2 + CO \longrightarrow Na_2CO_3$$

8. Na_2O_2, on being heated with nitric oxide, produces nitrate.

$$Na_2O_2 + \underset{\text{Nitric oxide}}{2\,NO} \longrightarrow \underset{\text{Sodium nitrite}}{2NaNO_2}$$

9. Na_2O_2 reacts with sulphur dioxide to form sodium sulphate.

$$Na_2O_2 + SO_2 \longrightarrow Na_2SO_4$$

10. Na_2O_2 is diamagnetic and is regarded as a salt of dibasic acid, H_2O_2.

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

Uses:

1. Sodium peroxide is used as an oxidising agent in laboratory.
2. It is used as a bleaching agent because of its oxidising property. It is used for bleaching delicate fibres such as silk, straw, leathers etc.
3. It is used for purification of air in confined spaces such as submarines. It combines with CO_2 to form sodium carbonate and oxygen.

$$2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + O_2\uparrow$$

4. It is used in the manufacture of dyes and any other chemicals such as benzoyl peroxide, sodium perborate etc.

4.10.2 Sodium Oxide [Na_2O]

Preparation:

1. It is formed when sodium is heated in regulated supply of air at 180°C and distilling the excess of the metal in vacuum.

$$2Na + \frac{1}{2}O_2 \longrightarrow Na_2O$$

2. Industrially, it is prepared by heating sodium nitrate or sodium nitrite with sodium.

$$2NaNO_3 + 10Na \xrightarrow{\Delta} 6Na_2O + N_2$$

$$2NaNO_2 + 6Na \xrightarrow{\Delta} 4Na_2O + N_2$$

3. Pure sodium oxide is formed by heating the mixture of sodium azide and sodium nitrite .

$$3NaN_3 + NaNO_2 \xrightarrow{\Delta} \underset{\text{(Pure)}}{2Na_2O} + 5N_2$$

Properties:

1. Na_2O is a colourless ionic solid and its aqueous solutions is a strong base.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

2. When Na_2O is heated above 400°C, it forms Na_2O_2 and metallic sodium vapours.

$$2Na_2O \xrightarrow{>400^\circ C} \underset{\text{Sodium peroxide}}{Na_2O_2} + 2Na$$

3. It reacts with water violently forming sodium hydroxide (caustic soda).

$$Na_2O + H_2O \longrightarrow 2NaOH + \text{Heat}$$

4. It reacts with liquid ammonia to give sodamide ($NaNH_2$).

$$Na_2O + NH_3 \longrightarrow NaNH_2 + NaOH$$

5. It burns in carbon dioxide to give sodium carbonate.

$$Na_2O + CO_2 \longrightarrow Na_2CO_3$$

Uses: It is used as a dehydrating and polymerising agent in organic chemistry.

4.10.3 Sodium Hydroxide (NaOH)

Common name: Caustic soda

Preparation: Commercially NaOH is prepared by the following methods:

1. **Causticising process or lime–caustic soda process:** By heating 10% Na_2CO_3 solution with milk of lime [$Ca(OH)_2$],

$$Na_2CO_3 + Ca(OH)_2 \xrightarrow{\Delta} 2NaOH + CaCO_3\downarrow$$

Calcium carbonate ($CaCO_3$), being slightly soluble, separates out as mud. The proceses is called **causticisation** or **caustication**.

2. **Electrolytic process:** Caustic soda, nowadays is manufactured by electrolysis of aqueous solution of sodium choride (brine).

Advantage of electrolytic process over causticising process:

- NaOH produced is highly pure.
- Hydrogen and chlorine are obtained as valuable by-products.

Theory : Brine solution contains $Na^{\oplus}$, $Cl^{\ominus}$, $H^{\oplus}$, $\overset{\ominus}{O}H$ ions.

$$NaCl \rightleftharpoons Na^{\oplus} + Cl^{\ominus}$$

$$H_2O \rightleftharpoons H^{\oplus} + \overset{\ominus}{O}H$$

On passing electron current through the solution, $Na^{\oplus}$ and $H^{\oplus}$ ions move towards the cathode. $H^{\oplus}$ ions are able to accept electron much more easily than $Na^{\oplus}$, as a result hydrogen (H_2) is liberated with the decomposition of more water molecules while $Na^{\oplus}$ ions remain in solution.

At anode, the $Cl^{\ominus}$ ions give up their electrons in preference to $\overset{\ominus}{O}H$ ions and Cl_2 gas is liberated.

At cathode: $2H^{\oplus} + 2e^- \rightarrow H_{2(g)}$

or

$$2H_2O + 2e^{\ominus} \longrightarrow H_2 + 2\overset{\ominus}{O}H$$

At anode: $2Cl^{\ominus} \longrightarrow Cl_2 + 2e^-$

The overall ionic equation is:

$$2Na^{\oplus} + 2Cl^{\ominus} + 2H_2O \longrightarrow 2Na^{\oplus} + 2\overset{\ominus}{O}H + H_{2(g)} + Cl_{2(g)}$$

If NaOH and Cl_2 so produced are allowed to come in contact they will react again as follows:

$$NaOH + Cl_2 \longrightarrow NaCl + NaClO + H_2O$$

To prevent the reaction between NaOH and Cl_2, it is necessary to separate anode from the cathode. This is accomplished by using diaphragm cells such as (a) Nelson diaphragm cell, (b) Castner–Kellner cell or mercury cathode cell and (c) Nafion membrane cell.

1. **Nelson diaphragm cell**: It consists of U-shaped perforated steel cathode lined inside with asbestos, and suspended in a rectangular iron tank. A carbon rod suspended into it acts as anode (Fig. 4.7). The electrolyte used is brine solution. The asbestos lining separates the anode and the cathode. The steam blown from the bottom during the process, helps in keeping the electrolyte warm and the perforations clear.

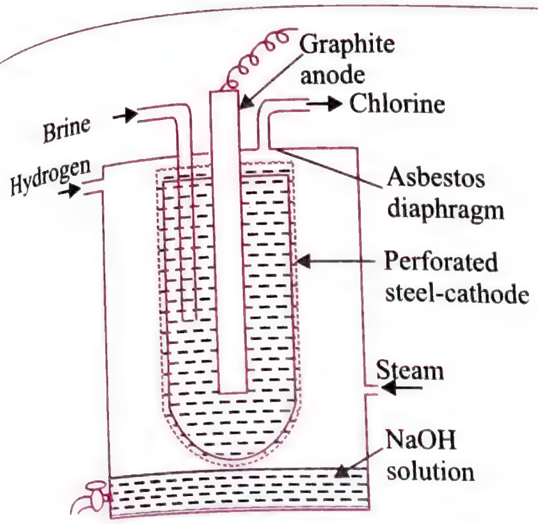


Fig. 4.7 Nelson cell for the production of NaOH

Electrolyte: Brine solution

Cathode: Perforated steel

Anode: Carbon(graphite) rod

In solution:

$NaCl \rightleftharpoons Na^{\oplus} + Cl^{\ominus}$

$H_2O \rightleftharpoons H^{\oplus} + OH^{\ominus}$

At cathode: $2H^{\oplus} + 2e^{-} \longrightarrow H_2$

(Or) $2H_2O + 2e^{-} \longrightarrow H_2 + 2\overset{\ominus}{O}H$

At anode: $2Cl^{\ominus} \longrightarrow Cl_2 + 2e^{-}$

Overall ionic equation:

$$2Na^{\oplus} + 2Cl^{\ominus} + 2H_2O \longrightarrow 2Na^{\oplus} + 2\overset{\ominus}{O}H + Cl_2 + H_2$$

Note: This cell is used for industrial preparation of Cl_2.
This cell is also used for production of Na_2CO_3, when CO_2 is mixed with steam.

2. **Castner–Kellner cell or mercury cathode cell:** It consists of a large rectangular tank divided into three compartments by slate partitions which do not touch the bottom of the tank (Fig. 4.8). The slate partitions are suspended in mercury placed at the bottom of the tank. Thus mercury in one compartment can flow into the other, but the solution present in any of the compartment cannot flow into the other.

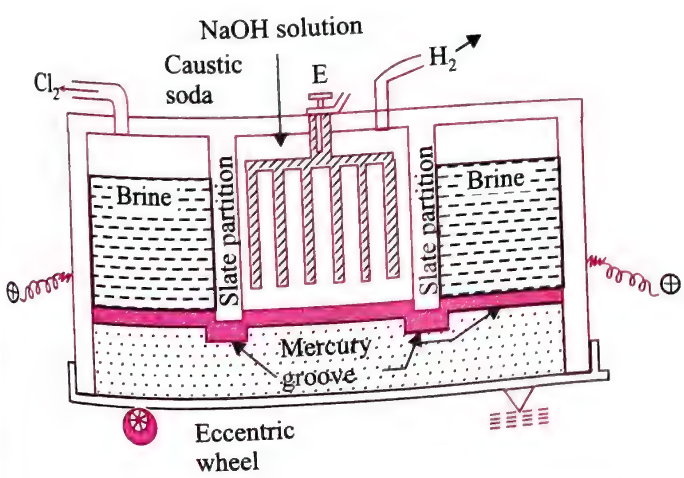


Fig. 4.8 Castner–Kellner cell for the production of NaOH

Brine is placed in the outer two compartments, whereas central compartment contains dilute NaOH solution.

On passing current, electrolysis takes place in the outer and central compartments as given below:

Outer compartments:

$NaCl \longrightarrow Na^{\oplus} + Cl^{\ominus}$

$H_2O \rightleftharpoons H^{\oplus} + \overset{\ominus}{O}H$

$Na^{\oplus}$ and $H^{\oplus}$ ions migrate towards mercury cathode, whereas $Cl^{\ominus}$ and $\overset{\ominus}{O}H$ migrate towards graphite anode.

At anode: $2Cl^{\ominus} \longrightarrow Cl_2 + 2e^{-}$

Because the discharge potential of $Cl^{\ominus}$ ion is lower than that of $\overset{\ominus}{O}H$ ions, $Cl^{\ominus}$ ion gives up its electron in preference to $\overset{\ominus}{O}H$ ions, and Cl_2 gas is liberated at anode, while $\overset{\ominus}{O}H$ ions remain in the solution.

At cathode: $Na^{\oplus} + e^{-} \longrightarrow Na$

$$Na + Hg \longrightarrow \underset{\text{Sodium amalgam}}{NaHg}$$

Sodium amalgam passes into the central compartment due to the rocking motion given to the cell by the eccentric wheel.

Central compartment:

$$NaOH \longrightarrow Na^{\oplus} + \overset{\ominus}{O}H \quad \text{...(4.7)}$$

$$H_2O \rightleftharpoons H^{\oplus} + \overset{\ominus}{O}H \quad \text{...(4.8)}$$

NaOH, being strong electrolyte, undergoes complete dissociation, whereas H_2O being a weak electrolyte, gets partially ionised.

$H^{\oplus}$ and $Na^{\oplus}$ ions migrate towards cathode, whereas $\overset{\ominus}{O}H$ ions migrate towards anode.

At anode: $\overset{\ominus}{O}H \longrightarrow OH + e^{-}$

$$NaHg + OH \longrightarrow NaOH + Hg$$

$\overset{\ominus}{O}H$ ions migrate towards anode and combine with sodium amalgam to form NaOH.

At cathode: $2H^{\oplus} + 2e^{\ominus} \longrightarrow H_{2(g)}$

Because discharge potential of $H^{\oplus}$ is lower than that of $Na^{\oplus}$ ions, $H^{\oplus}$ ions are thus discharged at the cathode and H_2 is liberated.

As $H^{\oplus}$ ions are continuously discharged at the cathode, the equilibrium (4.8) shifts towards the right thereby producing more of $\overset{\ominus}{O}H$ ions. The $OH^{\ominus}$ ions, thus produced react with sodium amalgam forming more and more of NaOH. When the solution of NaOH is sufficiently concentrated (~ 20%), it is drawn out, evaporated, fused and cast into sticks.

3. **Nafion membrane cell:** The natural brine (NaCl) is now electrolysed in a membrane cell in which anolyte and catholyte are separated by a Nafion membrane (Fig. 4.9). Nafion is a copolymer of tetrafluoro-ethylene and perfluoro sulphoryl ethoxyether. The copolymer is supported by a Teflon mesh.

$$2NaCl_{(aq)} + H_2O \xrightarrow{\text{Electrolysis}} 2NaOH_{(aq)} + H_{2(g)}\uparrow + Cl_{2(g)}\uparrow$$

Nafion membrane allows $Na^{\oplus}$ ions to migrate from one half cell to another but prevents mixing of gaseous products.

Nafion membrane cell is also used in the preparation of Cl_2, KOH from electrolysis of KCl.

Advantages of Nafion membrane cell over other methods:

a. Mercury and asbestos used in other methods are neither environment-friendly nor economical, whereas Nafion membrane serves both the purpose.

b. Purity of NaOH produced is much higher.

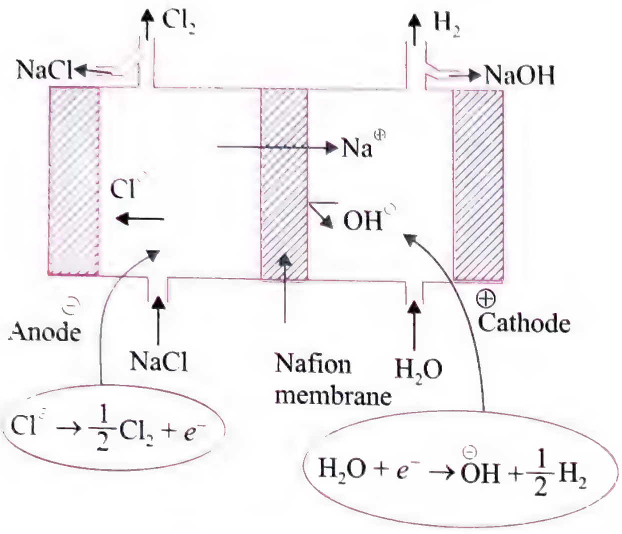


Fig. 4.9 Nafion membrane cell

Properties:

1. Sodium hydroxide is a deliquescent solid, and readily absorbs moisture and carbon dioxide from the atmosphere.

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

2. NaOH is highly soluble in water and the process of dissolution is exothermic.

$$NaOH \longrightarrow Na^{\oplus} + {}^{\ominus}OH$$

3. It decomposes to its elements at 1300°C

$$2NaOH \xrightarrow[\Delta]{1300°C} 2Na + H_2 + O_2$$

4. Reaction with acids and acidic oxides: It reacts with acids and acidic oxides to form salts.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$
$$NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O$$
$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$
$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$
$$2NaOH + SiO_2 \longrightarrow Na_2SiO_3 + H_2O$$

5. Reaction with non-metals:

$$2NaOH \text{ (cold and conc)} + Br_2 \longrightarrow NaBr + NaOBr + H_2O$$
$$6NaOH \text{ (hot and conc)} + 3Br_2 \longrightarrow 5NaBr + NaBrO_3 + 3H_2O$$
$$3NaOH + P_4 + 3H_2O \xrightarrow{\Delta} 3NaH_2PO_2 + PH_3 \text{ (Phosphine)}$$
$$6NaOH + 4S \xrightarrow{\Delta} \underset{\text{Sodium sulphide}}{2Na_2S} + \underset{\text{Sodium thiosulphate}}{Na_2S_2O_3} + 3H_2O;$$
$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$

6. Reaction with ammonium salts: It reacts with ammonium salts to give off ammonia.

$$NH_4Cl + NaOH \longrightarrow NH_3\uparrow + NaCl + H_2O$$
$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3\uparrow + 2H_2O$$

7. Reaction with metals: It reacts with metals such as Cu, Fe, Ag etc. It also reacts with metals such as Sn, Al, Zn which are amphoteric (to form amphoteric oxides).

$$Zn + 2NaOH \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2\uparrow$$
$$2Al + 2NaOH + 2H_2O \longrightarrow \underset{\text{Sodium meta aluminate}}{2NaAlO_2} + 3H_2\uparrow$$
$$Sn + 2NaOH \longrightarrow \underset{\text{Sodium stannite}}{Na_2SnO_2} + H_2\uparrow$$
$$Sn + \underset{\text{(excess)}}{2NaOH} + H_2O \longrightarrow \underset{\text{(Sodium stannate)}}{Na_2SnO_3} + 2H_2$$

8. Reaction with salts: NaOH dissolves acidic or amphoteric salts (oxides).

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$
$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

a. It forms metallic hydroxides.

$$FeCl_3 + 3NaOH \longrightarrow Fe(OH)_3 + 3NaCl$$

Similar reaction occurs with $CuSO_4$, $FeSO_4$ and $MnSO_4$.

b. When hydroxides are unstable, the oxides are precipitated.

$$HgCl_2 + 2NaOH \longrightarrow Hg(OH)_2 + 2NaCl$$
$$Hg(OH)_2 \longrightarrow \underset{\text{Yellow ppt}}{HgO\downarrow} + H_2O$$
$$2AgNO_3 + 2NaOH \longrightarrow \underset{\text{Brown ppt}}{Ag_2O\downarrow} + 2NaNO_3 + H_2O$$

c. With salts of amphoteric metals such as Pb, Sn, As, Sb, Al, Zn, first hydroxide is formed. In excess of NaOH, hydroxide dissolves.

$$Pb(NO_3)_2 + 2NaOH \longrightarrow Pb(OH)_2 + 2NaNO_3$$
$$Pb(OH)_2 + 2NaOH \longrightarrow Na_2PbO_2 + 2H_2O$$

Similar reaction occurs with $SnCl_2$, $Al_2(SO_4)_3$ and $ZnSO_4$

d. With Hg_2^{2+} (mercurous) and Hg^{2+} (mercuric), the precipitate of their oxides are formed.

$$Hg_2(NO_3)_2 + 2NaOH \longrightarrow 2NaNO_3 + H_2O + Hg_2O\downarrow$$
$$Hg(NO_3)_2 + 2NaOH \longrightarrow 2NaNO_3 + H_2O + HgO\downarrow$$

Uses:

1. In manufacture of soap, paper and viscose rayon (artificial silk).
2. In manufacture of organic dye stuffs.
3. As laboratory reagent.
4. In petroleum industry for refining.
5. In the preparation of pure fats and oils.
6. In the purification of bauxite.
7. In textile industry for mercarising cotton fabrics.

ILLUSTRATION 4.20

Why a standard solution of NaOH cannot be prepared by direct weighing cold NaOH?

Sol. NaOH is deliquescent and reacts with atmospheric CO_2 to form Na_2CO_3, thus NaOH is not pure but contains impurity of Na_2CO_3.

4.10.4 Sodium Chloride (NaCl)

Preparation: The most abundant source of sodium chloride is sea water which contains 2.7–2.9% by mass of the salt. In tropical countries, like India, common salt is generally obtained by *evaporation of sea water*. In India, approximately 50 lakh tons of salt are produced annually by solar evaporation.

Crude sodium chloride obtained by *crystallisation of brine solution* contains sodium sulphate (Na_2SO_4), calcium sulphate ($CaSO_4$), calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$) as impurities. $CaCl_2$ and $MgCl_2$ are deliquescent (absorb moisture easily from the atmosphere), therefore impure common salt gets wet in rainy season.

To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with hydrogen chloride (HCl) gas. Crystals of pure sodium chloride separate out, whereas calcium chloride and magnesium chloride being more soluble remain in the solution. The remaining solution or wash liquid is known as **bittern**. It contains in concentrated form of the calcium and magnesium chlorides, bromides, iodides and other chemicals originally present in brine. It is a commercial source of magnesium compounds–magnesium sulphate (Epsom salt), $MgCl_2$ and $MgBr_2$.

Properties:

1. Sodium chloride is colourless, crystalline substance (cubic crystals) with melting point 1081K.
2. Sodium chloride has a solubility of 36.0 g in 100 g of water at 273 K. However, the solubility does not vary appreciably with rise or fall of temperature.
3. At a temperature of 273–252 K, it exists as a dihydrate, $NaCl{\cdot}2H_2O$.
4. NaCl is not hygroscopic, but ordinary salt is slightly hygroscopic due to traces of magnesium and calcium chloride present in it.
5. On heating with conc H_2SO_4, NaCl produces HCl.
$$NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + HCl$$
6. On heating with conc H_2SO_4 and MnO_2, NaCl produces Cl_2. $2NaCl + 2H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$

Uses:

1. It is used as a common salt or table salt for domestic purposes.
2. It is used as a preservative, e.g. in packing and curing of meat and fish.
3. It is used as a starting material in the preparation of Na_2O_2, NaOH, Na_2CO_3 etc.
4. It is used as a freezing mixture (mixture of NaCl and ice).

4.10.5 Sodium Hydrogen Carbonate ($NaHCO_3$)

Statement: Sodium hydrogen carbonate or sodium bicarbonate is also known as *baking soda*.

Explanation: Sodium hydrogen carbonate on heating decomposes to give bubbles of carbon dioxide (CO_2) (leaving holes in cakes, pastries etc. and makes them light and fluffy).

$$2NaHCO_3 \xrightarrow[375\,K]{\Delta} Na_2CO_3 + CO_2\uparrow + H_2O$$

Preparation: Sodium hydrogen carbonate ($NaHCO_3$) is prepared by saturating a solution of sodium carbonate (Na_2CO_3) with carbon dioxide (CO_2). Sodium hydrogen carbonate being sparingly soluble in water, gets separated out as white crystalline powder. It is washed with cold water and dried in air.

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$$

Properties:

1. White crystalline powder, sparingly soluble in water.
2. Solution of sodium hydrogen carbonate is alkaline.
$$HCO_3^{\ominus} + H_3O \rightleftharpoons H_2CO_3 + \overset{\ominus}{O}H$$
Or $NaHCO_3 + H_2O \rightleftharpoons H_2CO_3 + NaOH$
3. $NaHCO_3$ decomposes at 375 K to give carbon dioxide
$$NaHCO_3 \xrightarrow{375\,K} Na_2CO_3 + CO_2 + H_2O$$
4. It is amphi-protic
$$HCO_3^{\ominus} + H^{\oplus} \longrightarrow H_2CO_3 \quad \text{(Proton acceptor)}$$
$$HCO_3^{\ominus} \longrightarrow H^{\oplus} + CO_3^{2-} \quad \text{(Proton donor)}$$
5. With metal salts, is forms corresponding carbonate.
$$ZnSO_4 + 2\,NaHCO_3 \longrightarrow ZnCO_3 + Na_2SO_4 + H_2O + CO_2$$

Uses:

1. It is used in the preparation of baking powder. Baking powder is a mixture of $NaHCO_3$ (30%), starch (40%), calcium dihydrogen phosphate [$Ca(H_2\,PO_4)_2$] (10%) and sodium aluminum sulphate, [$NaAl(SO_4)_2$] (20%). The $Ca(H_2PO_4)_2$ is acidic and when moistened it reacts with $NaHCO_3$, giving CO_2. Starch is used as a filler [$NaAl\,(SO_4)_2$] to slow down the reaction so that CO_2 is given off more slowly.
2. In medicines, used as an *antacid*, as it neutralises the acidity in the stomach.
3. It is used in fire extinguishers to produce CO_2.
$NaHCO_3 + HCl \longrightarrow NaCl + CO_2\uparrow + H_2O$
4. It is used as a mild antiseptic for skin infections.

4.10.6 Sodium Carbonate ($Na_2CO_3{\cdot}10H_2O$)

Common name: Washing soda or sal soda

Other forms of sodium carbonate:

Na_2CO_3	Anhydrous	Soda-ash or soda
$Na_2CO_3{\cdot}H_2O$	Monohydrate	Crystal carbonate
$Na_2CO_3{\cdot}7H_2O$	Heptahydrate	

Preparation: *Solvay ammonia process*: Sodium carbonate is manufactured on industrial scale by Solvay ammonia process. The process has been named after the belgian chemist, Ernest Solv-

Principle: It is based on the formation of sparingly soluble sodium hydrogen carbonate ($NaHCO_3$) when CO_2 is passed through brine solution (sodium chloride solution) saturated with ammonia. $NaHCO_3$ is finally calcined to form sodium carbonate (Na_2CO_3).

Procedure: When CO_2 is passed through brine (sodium chloride solution) saturated with ammonia, sodium bicarbonate ($NaHCO_3$) is formed.

$$NH_3 + H_2O \longrightarrow NH_4OH \rightleftharpoons NH_4^{\oplus} + {}^{\ominus}OH$$
$$CO_2 + H_2O \longrightarrow H_2CO_3 \rightleftharpoons H^{\oplus} + HCO_3^{\ominus}$$
$$NH_3 + CO_2 + 2H_2O \longrightarrow NH_4HCO_3 + H_2O$$
or
$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$$
$$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3\downarrow + NH_4Cl$$

Ammonium chloride remains in solution, whereas sodium hydrogen carbonate, which is not very soluble in the presence of NaCl (due to common ion effect) is filtered and heated/calcined to produce sodium carbonate.

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

The sodium carbonate obtained in this way is contaminated with ammonium salts. It is purified by blowing carbon dioxide through its aqueous solution. The sodium hydrogen carbonate formed in this way is filtered and heated to give pure sodium carbonate. Recrystallisation from water produces washing soda ($Na_2CO_3 \cdot 10H_2O$).

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$$
$$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

Function of ammonia:

CO_2 is slighty soluble in water.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
$$H_2CO_3 \rightleftharpoons H^{\oplus} + HCO_3^{\ominus}$$

As a result, concentration of H_2CO_3 is low. Further, because H_2CO_3 is a weak acid, it gets feebly ionised and thus the concentration of $HCO_3^{\ominus}$ is low.

To shift the equilibrium in the forward direction, when a base such as NH_3 is added, it combines with $H^{\oplus}$ to form $NH_4^{\oplus}$ ions.

$$NH_3 + H^{\oplus} \longrightarrow NH_4^{\oplus}$$

Thus, the function of NH_3 is to produce a sufficient amount of $HCO_3^{\ominus}$ ions which enable sparingly soluble $NaHCO_3$ to precipitate out.

Various steps involved in the Solvay–ammonia process are as follows:

1. **Saturation of brine with ammonia:** Saturation of brine (NaCl solution) is done in *ammonia absorber* (Fig. 4.10). Ammonia from ammonia generator is bubbled through the brine solution and this then rises up the absorption tower down which a stream of brine flows over perforated shelves. The ammoniacal brine so produced is allowed to stand for sometime so that hydroxides of calcium, magnesium etc. settle down. The clear liquid is cooled thoroughly and then it goes into carbonation tower.

$$2\,NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2\,CO_3$$
$$MgCl_2 + (NH_4)_2\,CO_3 \longrightarrow MgCO_3\downarrow + NH_4Cl$$
$$MgCl_2 + 2NH_4OH \longrightarrow Mg(OH)_2\downarrow + 2NH_4Cl$$

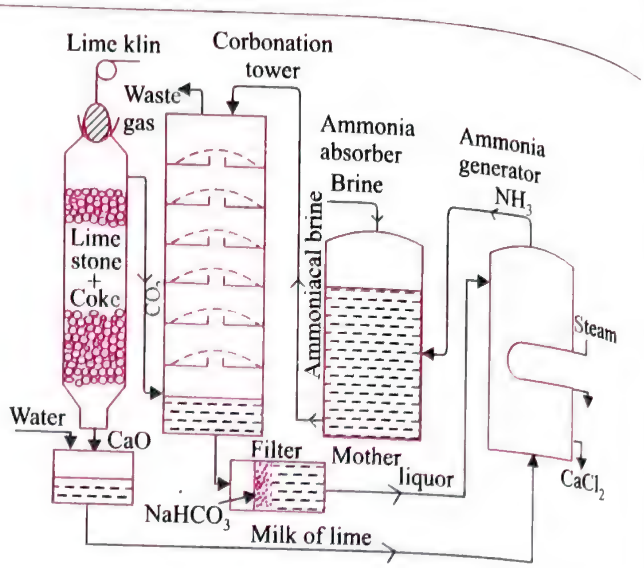


Fig. 4.10 Solvay's ammonia process for the manufacture of sodium carbonate

2. **Carbonation**: Carbonation tower consists of a number of compound diaphragms, each made up of horizontal iron plate with a hole in the centre and over this a curved plate perforated all over and deeply cut into grooves around the circumference is placed. CO_2 rises up from the base of the tower and is brought in contact with ammoniated brine at each compound diaphragm. The $NaHCO_3$, thus formed, is sparingly soluble in brine and therefore separates out.

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$$
$$NH_4HCO_3 + NaCl \longrightarrow Na\,HCO_3 + NH_4Cl$$

3. **Filtration:** The thick liquid obtained from the carbonation tower is passed through a rotary vacuum filter and $NaHCO_3$ left behind on the filter cloth is scraped off from time to time.
4. **Calcination**: The $NaHCO_3$ obtained above is ignited in specially constructed cylindrical vessels and CO_2 produced is collected and reused.

$$2\,NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

5. **Ammonia recovery**: The mother liquor containing NH_4Cl flows down the ammonia recovery tower where it is heated with slaked lime, $Ca(OH)_2$.

$$NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2NH_3 + 2H_2O$$

Ammonia, thus is set free, goes to the ammonia absorber tower. Slaked lime, required in ammonia recovery process, and CO_2, required in carbonation process, are obtained as follows :

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$
$$CaO + H_2O \longrightarrow Ca(OH)_2$$

The Solvay process is very economical because, except for NaCl and $CaCO_3$, other raw materials used in the process are not consumed. Thus:

1. Quicklime and ammonia formed are reacted to produce ammonia, so that apart from making up of small losses, no additional ammonia is required.
2. Carbon dioxide formed is reintroduced into the tower.
3. NaCl and $CaCO_3$ are cheap materials, calcium chloride is obtained as a by-product which finds no large-scale industrial applications.

Thus the process is self-contained (shown in Fig. 4.11), economical and continuous.

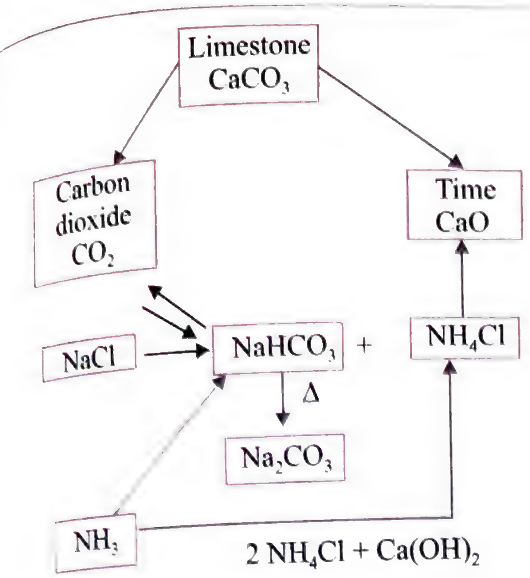


Fig. 4.11 Flow diagram for Solvay–ammonia process

Properties:

1. Sodium carbonate is a white crystalline solid and exists as decahydrate, i.e. $Na_2CO_3{\cdot}10H_2O$.
2. Reaction with water: It is readily soluble in water with the evolution of considerable amount of heat. Na_2CO_3 being a salt of a strong base (NaOH) and a weak acid (H_2CO_3), when dissolved in water undergoes hydrolysis to form an alkaline solution.

$$Na_2CO_3 + 2H_2O \longrightarrow H_2CO_3 + 2NaOH$$

$$\text{or } CO_3^{2-} + H_2O \longrightarrow HCO_3^{\ominus} + 2\overset{\ominus}{O}H$$

3. Action of heat: On heating (below 375 K), it loses water of crystallisation to form monohydrate ($Na_2CO_3{\cdot}H_2O$). Above 375 K, monohydrate changes to amorphous white powder known as *soda ash*.

$$Na_2CO_3{\cdot}10H_2O \xrightarrow{<375\text{ K}} Na_2CO_3{\cdot}H_2O + 9H_2O$$

$$Na_2CO_3{\cdot}H_2O \xrightarrow{>375\text{ K}} \underset{\substack{\text{Soda ash or}\\ \text{anhydrous}\\ \text{sodium carbonate}}}{Na_2CO_3} + H_2O$$

4. Reaction with acids: It react with dilute mineral acids producing effervescence due to evolution of CO_2 gas.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2\uparrow$$

$$\text{Or } CO_3^{2-} + 2H^{\oplus} \longrightarrow H_2O + CO_2\uparrow$$

5. Reaction with metal salts: With metal salts, it forms normal or basic carbonate or hydroxide.

$$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3 + 2NaCl$$

$$2\ Na_2CO_3 + 2MgCl_2 + H_2O \longrightarrow MgCO_3{\cdot}Mg(OH)_2 + 4NaCl + CO_2$$

$$3\ Na_2CO_3 + Fe_2(SO_4)_3 \longrightarrow Fe_2(CO_3)_3 + 3Na_2SO_4$$

6. Reaction with CO_2: On passing CO_2 through conc solution of Na_2CO_3, $NaHCO_3$ gets precipitated.

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$$

7. Reaction with silica: When mixture of Na_2CO_3 and silica (SiO_2) is fused, sodium silicate is formed.

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2\uparrow$$

Sodium silicate is also known as **water glass** or **soluble glass** as it is soluble in water.

8. When aqueous solution of Na_2CO_3 containing sulphur is treated with sulphur dioxide, sodium thiosulphate is formed.

$$Na_2CO_3 + SO_2 + H_2O \longrightarrow \underset{\text{Sodium sulphite}}{Na_2SO_3} + CO_2\uparrow$$

$$Na_2SO_3 + S \longrightarrow \underset{\text{Sodium thiosulphate}}{Na_2S_2O_3}$$

Uses:

1. It is used in the manufacture of glass, water glass, caustic soda and borax.
2. It is used for softening of hard water, as carbonates of magnesuim and calcium are water insoluble.

$$CO_3^{2-} + Mg^{2+} \longrightarrow MgCO_3\downarrow$$

$$CO_3^{2-} + Ca^{2+} \longrightarrow CaCO_3\downarrow$$

3. It is used in laundry as washing soda because on hydrolysis, it gives NaOH (an alkali).
4. It is used in paper, paints and textile industry.
5. It is used as an important laboratory reagent both in qualitative and quantitative analysis.

ILLUSTRATION 4.21

Why potassium carbonate (K_2CO_3) cannot be prepared by Solvay–ammonia process?

Sol. Potassium carbonate cannot be prepared by Solvay–ammonia process because $KHCO_3$ is highly soluble in water. Thus, when CO_2 is passed through ammoniated solution of KCl, $KHCO_3$ does not get precipitated and hence cannot be separated.

4.10.7 Sodium Sulphate (Na_2SO_4)

Common name: Salt cake

Other forms of sodium sulphate:

$Na_2SO_4{\cdot}10H_2O$	Decahydrate	Glauber's salt
$Na_2SO_4{\cdot}7H_2O$	Heptahydrate	

Preparation:

1. The anhydrous salt, known as salt cake, is prepared on the industrial scale by heating strongly sodium chloride with conc. sulphuric acid.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl\uparrow$$

$$NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl\uparrow$$

2. If aqueous solution of Na_2SO_4 is cooled below 32°C, Glauber's salt $Na_2SO_4{\cdot}10H_2O$ separates out. However, if cooling is done below 12°C, $Na_2SO_4{\cdot}7H_2O$ crystals are formed.

Properties:

1. It is a colourless crystalline salt.
2. In dry air, $Na_2SO_4{\cdot}10H_2O$ effloresces forming anhydrous Na_2SO_4.

$$Na_2SO_4{\cdot}10H_2O \xrightarrow{\text{Dry air}} Na_2SO_4 + 10H_2O$$

Uses:

1. It is used in glass and paper industry.
2. In making ultramarines.
3. In medicines as purgative.

4.10.8 Microcosmic Salt [$Na(NH_4)HPO_4$]

Preparation: It is prepared by dissolving ammonium chloride and disodium hydrogen phosphate in hot water. On cooling, the crystals of salt separate out.

$$NH_4Cl + Na_2HPO_4 \longrightarrow Na(NH_4)HPO_4 + NaCl$$

Properties:

1. It is a colourless crystalline solid, sparingly soluble in water.
2. On heating it forms metaphosphate, a glassy mass. Hence, it can also be used as borax, in bead test known as **microcosmic bead test.**

$$Na(NH_4)HPO_4 \longrightarrow NH_3 + H_2O + \underset{\text{(Metaphosphate, glassy bead)}}{NaPO_3}$$

$$CuO + NaPO_3 \longrightarrow \underset{\text{(Orthophosphate, blue bead)}}{CuNaPO_4}$$

Uses: It is used for testing silica with which a cloudy bead containing floating property of silica is obtained.

4.11 SOME IMPORTANT COMPOUNDS OF POTASSIUM (K)

4.11.1 Potassium Peroxide (K_2O_2)

Preparation: Controlled oxidation of potassium in excess air or oxygen at 300°C gives mainly K_2O_2.

$$2K + O_2 \xrightarrow{300\,C} K_2O_2$$

Properties: It gives H_2O_2 when dissolved in water.

$$K_2O_2 + 2H_2O \longrightarrow 2KOH + H_2O_2$$

4.11.2 Potassium Superoxide (KO_2)

Preparation:

1. It is prepared by burning potassium in excess of oxygen or air free from moisture.

$$K + O_2 \longrightarrow KO_2$$

2. It is prepared by prolonged action of oxygen on a solution of the metal in liquid ammonia.

$$\underset{\text{(Blue)}}{K} \xrightarrow[O_2]{\text{liq.}NH_3} \underset{\text{(White)}}{K_2O_2} \xrightarrow{O_2} \underset{\text{(Red)}}{K_2O_3} \xrightarrow{O_2} \underset{\text{(Deep yellow)}}{KO_2}$$

3. It is obtained by reacting dry potassium hydroxide with ozone.

$$2KOH + O_3 \longrightarrow 3KO_2 + H_2O$$

Properties:

1. It is an orange yellow solid which melts at high temperature to give a dark oily liquid.
2. It is paramagnetic due to one unpaired electron. Hence, its structure may be represented as $K^{\oplus}[O\text{–}O]^{\ominus}$.
3. It behaves as a very powerful oxidising agent. It reacts with water to give an alkaline solution containing H_2O_2.

$$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$$

4. On heating, it reacts with CO and CO_2, to give potassium carbonate and oxygen.

$$2KO_2 + CO \xrightarrow{\Delta} K_2CO_3 + O_2$$

$$2KO_2 + CO_2 \xrightarrow{\Delta} K_2CO_3 + \frac{3}{2}O_2$$

5. On heating with sulphur, it forms potassium sulphate.

$$2KO_2 + S \xrightarrow{\Delta} K_2SO_4$$

Uses:

1. As an oxidising agent.
2. As air purifier in space capsules, submarines and breathing masks as both produce oxygen and remove carbon dioxide.

4.11.3 Potassium Hydroxide (KOH)

Common name: Caustic potash

Preparation:

1. It can be obtained by boiling a solution of potassium carbonate with calcium hydroxide, leading to a double-decomposition reaction (metathesis reaction) which causes calcium carbonate to precipitate, leaving potassium hydroxide in solution.

$$Ca(OH)_2 + K_2CO_3 \longrightarrow CaCO_3\downarrow + 2KOH$$

2. It can also be manufactured by the electrolysis of KCl solution (similar to preparation of NaCl).

At cathode: $2K^{\oplus} + 2H_2O + 2e^{\ominus} \longrightarrow H_2 + 2KOH$

At anode: $2\,Cl^{\ominus} \longrightarrow Cl_2 + 2e^{\ominus}$

Properties:

1. The properties are similar to those of NaOH.
2. Alcoholic caustic potash is a useful reagent in organic chemistry.

$$C_2H_2Br + KOH_{(alc)} \longrightarrow CH_2{=}CH_2 + KBr + H_2O$$

Uses:

1. Alcoholic potash is used as a reagent in organic chemistry.
2. KOH is used as an absorbent for CO_2, for which purpose it is preferred over NaOH, since after absorption of CO_2, the $KHCO_3$ formed is soluble whereas $NaHCO_3$ being sparingly soluble separates out and chokes the CO_2 absorption bulbs.
3. In the meanfuacture of soft soap.
4. As a drying agent for basic gases, since it is extremely deliquescent.
5. In the Ni–Fe storage cell.

4.11.4 Potassium Carbonate (K_2CO_3)

Common name: Potash or pearl ash

Preparation:

1. It is made by extracting wood with water, filtering, evaporating to dryness followed by strong heating.
2. It can be made by heating potassium nitrate with carbon, extracting the calcined mass with water followed by filtration and evaporation.

$$4KNO_3 + 5C \longrightarrow 2K_2CO_3 + 3CO_2 + 2N_2$$

3. Engel and Precht's process (or magnesia process) involves reaction between KCl solution and solid hydrated magnesium carbonate, $MgCO_3 \cdot 3H_2O$ in the presence of CO_2 at 293 K.

$$3[MgCO_3 \cdot 3H_2O] + 2KCl + CO_2 \xrightarrow{293\text{ K}} 2[MgCO_3 \cdot KHCO_3 \cdot 4H_2O] + MgCl_2$$

The insoluble hydrated carbonate–bicarbonate double salt, crystallising out is separated and decomposed either by heating (at 410 K) water under pressure or by a cold suspension of MgO.

$$2[MgCO_3 \cdot KHCO_3 \cdot 4H_2O] \longrightarrow K_2CO_3 + 2MgCO_3 + 9H_2O + CO_2$$

$$2[MgCO_3 \cdot KHCO_3 \cdot 4H_2O] + MgO \longrightarrow 3[MgCO_3 \cdot 3H_2O] + K_2CO_3$$

The $MgCO_3$ precipitated is filtered off and used again while the filtrate is evaporated to yield K_2CO_3.

4. Potassium carbonate is also commercially made by the carbonation of caustic potash.

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

5. A recent process known as the thermite process or Goldschmidt process uses a mixture of K_2SO_4 and milk of lime in the presence of CO_2 at 220°C and 30 atm pressure.

$$K_2SO_4 + Ca(OH)_2 + 2CO_2 \longrightarrow 2HCOOK + CaSO_4\downarrow + O_2$$

The precipitated $CaSO_4$ is filtered off. The filtrate containing potassium formate is evaporated to dryness and calcined.

$$2HCOOK + O_2 \longrightarrow K_2CO_3 + H_2O + CO_2$$

Properties:

1. It is white, deliquescent solid, which is highly soluble in water.
2. Its properties resemble closely those of Na_2CO_3.
3. On heating to redness in steam, it gives off CO_2.

$$K_2CO_3 + H_2O \longrightarrow 2KOH + CO_2$$

4. Hot concentrated solution of K_2CO_3 in water at 280–300 K, deposit crystals of trihydrate, $K_2CO_3 \cdot 3H_2O$.

$$\underset{\text{Trihydrate}}{K_2CO_3 \cdot 3H_2O} \xrightarrow{370\text{ K}} \underset{\text{Monohydrate}}{K_2CO_3 \cdot H_2O} \xrightarrow{400\text{ K}} \underset{\text{Anhydrous}}{K_2CO_3}$$

Trihydrate $K_2CO_3 \cdot 3H_2O$ loses two water molecules at 370 K to form monohydrate $K_2CO_3 \cdot H_2O$, which becomes anhydrous at 400 K.

Uses:

1. In the manufacture of hard glass and soft soap.
2. Mixed with Na_2CO_3, it forms fusion mixture.
3. For the preparation of other potassium compounds.
4. As a drying agent for certain neutral and basic organic compounds.

4.11.5 Potassium Oxide (K_2O)

Preparation:

1. It is prepared by heating KNO_3 or KO_2 with potassium.

$$2KNO_3 + 10K \longrightarrow 6K_2O + N_2$$

$$KO_2 + 3K \longrightarrow 2K_2O$$

2. It may be obtained by oxidising potassium in a limited supply of oxygen or air.

$$4K + O_2 \longrightarrow 2K_2O$$

Properties: A light yellow solid, resembling Na_2O in its chemical properties. Thus it dissolves in water forming potassium hydroxide.

$$K_2O + H_2O \longrightarrow 2KOH$$

4.11.6 Potassium Chloride (KCl)

It occurs in Stassfurt deposits as carnallite: $KCl \cdot MgCl_2 \cdot 6H_2O$ and sylvines: KCl.

Preparation:

1. Stassfurt deposits containing carnallite are dug out, grounded and extracted with hot 20% $MgCl_2$ solution. In this solution, KCl dissolves but NaCl and $MgSO_4$ remain insoluble. By filtration and crystallisation, KCl is obtained leaving $MgCl_2$ in the mother liquor. A second crop of crystals obtained by further concentration of the mother liquor yields a low grade variety of KCl. The mother liquor now left over is recycled.
2. Sylvine is chiefly KCl plus some NaCl. It is dissolved in boiling water and crystallised to yield crystals of KCl. NaCl is left behind in the mother liquor.

Properties:

1. KCl is a colourless, crystalline solid, highly soluble in water.
2. Its chemical properties resemble NaCl.

Uses:

1. As a fertiliser.
2. In the preparation of certain potassium compounds.

4.11.7 Potassium Sulphate [K_2SO_4]

Preparation:

1. It occurs in Stassfurt potash deposits as schonite: $K_2SO_4 \cdot MgCl_2 \cdot 6H_2O$ and as kainite: $K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$. A hot saturated solution is cooled to obtain a double sulphate of potassium and magnesium. This is treated with KCl solution and concentrated to obtain sparingly soluble crystalline K_2SO_4.
2. K_2SO_4 may also be prepared by the reactions.

$$2KCl + H_2SO_4 \longrightarrow K_2SO_4 + 2HCl$$

$$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$$

Properties:

1. It is a colourless crystalline substance. Unlike $Na_2SO_4 \cdot 10H_2O$, it does not form a hydrate.

2. Its chemical properties are similar to those of Na_2SO_4. It forms double salts known as alums, e.g. $K_2SO_4{\cdot}Al_2(SO_4)_3\,24H_2O$.

Uses: For making hard glass, potash alum and as fertiliser.

4.11.8 Potassium Bicarbonate ($KHCO_3$)

Preparation: It is prepared by saturating cold, concentrated K_2CO_3 solution by CO_2 followed by crystallisation.

$$K_2CO_3 + H_2O + CO_2 \longrightarrow 2KHCO_3$$

Properties: Its chemical properties are similar to those of $NaHCO_3$. On heating, it decomposes to yield K_2CO_3.

$$2KHCO \xrightarrow{\Delta} K_2CO_3 + H_2O + CO_2$$

ALUMS

When a mixture of potassium sulphate and aluminium sulphate is dissolved in concentrated water, *a double salt* separates out in the form of crystals. The composition of this double salt corresponds to the formula $K_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$. This is known as *potash alum*. Such double sulphates having general formula $R_2SO_4{\cdot}M(SO_4)_3{\cdot}24H_2O$ are called alums. 'R' corresponds to monovalent cation Na, K and M is trivalent cation such as Al, Fe, Cr.

Examples:

$K_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$	Potash alum (common alum)
$K_2SO_4{\cdot}Cr_2(SO_4)_3{\cdot}24H_2O$	Chrome alum
$(NH_4)_2SO_4{\cdot}Fe_2(SO_4)_3{\cdot}24H_2O$	Ferric ammonium alum
$K_2SO_4{\cdot}Mn_2(SO_4)_3{\cdot}24H_2O$	Manganic alum

1. When alum contains aluminum as trivalent cation, then it is named after monovalent cation. For example, potash alum $K_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$.
2. When trivalent cation is not aluminium, then alum is named after both, e.g. $(NH_4)_2SO_4{\cdot}Fe_2(SO_4)_3{\cdot}24H_2O$ is called ferric ammonium alum.

Preparation: Alums are generally prepared by mixing the component sulphates in equimolar proportion in hot aqueous solution and allowing the double sulphate to crystallise.

Properties: Alums are isomorphous, i.e. any two different alums have the same crystalline form. Two different alums can be mixed in solution and form mixed crystals. The crystal of one alum can 'grow' in a saturated solution of the first. Crystals of alums are octahedral.

4.11.9 Potash Alum [$K_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$]

Preparation: This is made on a large scale from the mineral, alunite or alumstone $K_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}4Al(OH)_3$. This mineral is heated and dissolved in H_2SO_4. Further, the calculated amount of K_2SO_4 is added and then alum is crystallised.

Alternatively, powdered bauxite may be treated with H_2SO_4. Any ferric sulphate present is reduced to ferrous ion by BaS. After filtration, a calculated quantity of K_2SO_4 is added and the solution is crystallised.

As a third method, one may mention the roasting of alum shale (aluminium silicate) containing FeS_2 (iron pyrites) as impurity. The roasted mass is extracted with water; the correct amount of KCl is added to the filtered extract and crystallised.

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$$

$$Al_2O_3{\cdot}xSiO_2 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O + xSiO_2$$

(From oxidation of pyrites)

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow \underset{\text{Crystals of alum}}{K_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O}$$

Properties:

1. Alum forms colourless crystals with an astringent taste.
2. Its solution is acidic due to hydrolysis.
3. On heating it dissolves in its own water of crystallisation but at a higher temperature it loses all its water and forms a white porous mass known as burnt alum. At very high temperatures, it gives aluminium oxide.

Uses:

1. As a mordant in dyeing.
2. In the purification of water.
3. In the paper industry.
4. In the tanning industry.

ILLUSTRATION 4.22

a. Name the alkali metals which form superoxides on heating in excess of air.
b. Name the alkali metal which floats on water without any apparent reaction with it.
c. Name the main factor which is responsible for the anomalous behaviour of lithium.
d. What is the general name for element of group 1?
e. Give the name of the alkali metal which is radioactive.
f. Name the alkali metal which shows diagonal relationship with magnesium.
g. Name the alkali metal which acts as the strongest reducing agent in aqueous solution.

Sol.

a. K, Rb and Cs b. Lithium
c. Similarity in charge/radius ratio
d. Alkali metals e. Francium
f. Lithium g. Lithium

ILLUSTRATION 4.23

Explain why:

a. Lithium on being heated in air mainly forms the monoxide and not peroxide.
b. An aqueous solution of sodium carbonate gives alkaline test.

Sol.

a. $Li^{\oplus}$ ion is very small in size. It is stabilised more by smaller anion, i.e. oxide ion (O^{2-}) as compared to peroxide ion (O_2^{2-}).
b. An aqueous solution of sodium carbonate gives alkaline tests because Na_2CO_3 undergoes hydrolysis.

$$Na_2CO_3 + H_2O \longrightarrow NaHCO_3 + NaOH$$

or

$$CO_3^{2-} + H_2O \longrightarrow HCO_3^{\ominus} + {}^{\ominus}OH$$

ILLUSTRATION 4.24

The chemistry of lithium is very much similar to that of magnesium even though they are placed in different groups. Explain.

Sol. The ratio of charge to radius of lithium and magnesium is nearly the same, hence they have similar chemistry and show diagonal relationship.

ILLUSTRATION 4.25

Give reason:

a. $CaCl_2$ is added to NaCl in the electrolytic manufacture of sodium.

b. An aqueous solution of iodine becomes colourless, on adding excess of sodium hydroxide.

Sol.

a. Pure sodium chloride melts at about 800°C. At this temperature, both sodium and chlorine (products of electrolysis) are corrosive in nature. Sodium also forms metallic fog at this temperature. To remove these problems, the fusion temperature is reduced to 600°C by adding $CaCl_2$.

b. Sodium reacts with NaOH forming colourless compounds. Thus the colour of iodine disappears on adding NaOH.

$$NaOH + I_2 \longrightarrow \underbrace{\underset{\text{Sodium iodide}}{NaI} + \underset{\text{Sodium hypoiodite}}{NaIO}}_{\text{Colourless products}} + H_2O$$

ILLUSTRATION 4.26

What is the oxidation state of Cs in

a. Cs_2O_2 b. Cs_2O c. CsO_2

Sol.

a. Let the oxidation state of Cs in Cs_2O_2 is x. Since Cs_2O_2 contains a peroxide linkage (O_2^{2-}), the oxidation state of peroxide ion is $(-1 \times 2 = -2)$, therefore

$$2x - 2 = 0$$

$$\Rightarrow x = +1$$

Thus the oxidation state of Cs in Cs_2O_2 is +1.

b. Let the oxidation state of Cs in Cs_2O is 'x'. Since Cs_2O contains O^{2-} ion, the oxidation state of oxide ion is –2.

$$\therefore\ 2x - 2 = 0 \Rightarrow x = +1$$

Thus, the oxidation state of Cs in Cs_2O is + 1.

c. Let the oxidation state of Cs in CsO_2 is 'x'. Since CsO_2 contains superoxide ion $(O_2^{\ominus})$, the oxidation state of superoxide ion $(O_2^{\ominus})$ is –1. Therefore,

$$x - 1 = 0$$

$$x = +1$$

Thus, oxidation state of Cs in CsO_2 is +1.

ILLUSTRATION 4.27

Starting with sodium chloride how would you proceed to prepare (a) sodium metal, (b) sodium hydroxide and (c) sodium peroxide?

Sol.

a. Sodium metal is manufactured by electrolysis of a fused mixture of NaCl (40%) and $CaCl_2$ (60%) in Down's cell at 873 K using iron cathode and graphite anode. Na is liberated at the cathode while Cl_2 is evolved at the anode.

At cathode: $Na^{\oplus}_{(melt)} + e^{\ominus} \longrightarrow Na_{(l)}$

At anode: $2Cl^{\ominus}_{(melt)} \longrightarrow Cl_{2(g)} + 2e^{\ominus}$

ii. Sodium hydroxide is manufactured by electrolysis of an aqueous solution of NaCl (brine) in Castner–Kellner cell using the mercury cathode and the carbon anode. Sodium which is discharged at the cathode combines with mercury to form sodium amalgam. Cl_2 gas is evolved at the anode.

At cathode: $Na^{\oplus} + e^{\ominus} \longrightarrow \underset{\text{Sodium}}{Na}$

$$2\,Na + x\,Hg \longrightarrow \underset{\text{Sodium amalgam}}{Na_2Hg_x}$$

At anode: $2Cl^{\ominus} \longrightarrow Cl_2 + 2e^{\ominus}$

The sodium amalgam thus obtained is treated with water to form sodium hydroxide and hydrogen gas.

$$Na_2Hg_x + 2H_2O_2 \longrightarrow 2NaOH + xHg + H_2$$

c. Sodium peroxide is obtained by heating sodium in excess of air. The initially formed sodium oxide reacts with more O_2 to form Na_2O_2.

$$4\,Na + O_2 \longrightarrow 2\,Na_2O$$

$$4\,Na_2O + O_2 \longrightarrow 2\,Na_2O_2$$

ILLUSTRATION 4.28

What happens when:

a. Hot and concentrated NaOH solution reacts with I_2.

b. White phosphorus is heated with caustic soda.

c. Excess of caustic soda reacts with zinc sulphate solution.

d. Excess of caustic soda is added to $AlCl_3$ solution.

e. Sodium is heated strongly in oxygen and the product is treated with H_2SO_4.

Sol.

a. $\underset{\text{Hot and conc solution}}{2\,NaOH} + I_2 \longrightarrow NaI + NaIO + H_2O$

b. $\underset{\text{White phosphorous}}{P_4} + 3NaOH + 3H_2O \longrightarrow \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2} + \underset{\text{Phosphine}}{PH_3}$

c. $2NaOH + ZnSO_4 \longrightarrow \underset{\text{Sodium Sulphate}}{Na_2SO_4} + \underset{\text{Zinc hydroxide}}{Zn(OH)_2}$

d. $2NaOH + AlCl_{3(aq)} \longrightarrow Al\,(OH)_3 + 3NaCl$

e. $Na + O_2 \xrightarrow{\Delta} Na_2O_2$ (Sodium peroxide)

$$\underset{}{Na_2O_2} + H_2SO_4 \longrightarrow \underset{\text{Sodium sulphate}}{Na_2SO_4} + \underset{\text{Hydrogen peroxide}}{H_2O_2}$$

4.12 BIOLOGICAL IMPORTANCE OF SODIUM AND POTASSIUM

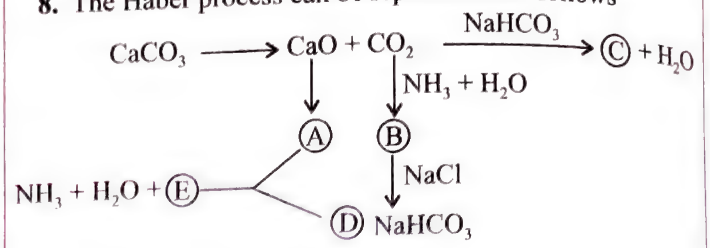
A typical 70 kg human being contains about 90 g of sodium (Na) and 170 g of potassium (K) as compared to 5 g of iron (Fe) and 0.06 g of copper (Cu).

The pair of major elements $Na^{\oplus}-K^{\oplus}$ are so similar chemically that it is surprising that they differ so greatly in their biological functions. While $Na^{\oplus}$ ions are found primarily outside the cells in blood plasma and other interstitial fluids, $K^{\oplus}$ ions are found inside the cells. Sodium ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into cells. Potassium ions activate many enzymes, participate in the oxidation of glucose to produce ATP (adenosine triphosphate) and along with sodium ions helps in the transmission of nerve signals.

There is a large difference in the concentration of sodium and potassium ions found on the opposite sides of the cell membrane. As an example, $Na^{\oplus}$ ions are present to the extent of 143 mmol L^{-1} in blood plasma, whereas concentration of $K^{\oplus}$ ions is only 5 mmol L^{-1} in RBC (red blood cells). These concentrations change to 10 mmol L^{-1} ($Na^{\oplus}$) and 105 mmol L^{-1} ($K^{\oplus}$). These ionic gradients known as sodium potassium (Na–K) pump operate across the cell membranes that consumes more than one-third of the ATP used by a resting animal and about 15 kg per 24 hours in a resting human being.

CONCEPT APPLICATION EXERCISE 4.1

1. Write three general characteristics of the *s*-block of the periodic table which distinguish them from the elements of other blocks.
2. The alkali metals follow the noble gases in their atomic structure. What properties of these metals can be predicted from this information.
3. Why is sodium metal kept under kerosene oil?
4. When is a cation highly polarising? Which alkali metal cation has the highest polarising power?
5. Why superoxides of alkali metals are paramagnetic?
6. Alkali metals are paramagnetic but their salts are diamagnetic. Explain.
7. Give reasons for the following:
   a. LiCl is more covalent than KCl.
   b. LiI has lower melting point than LiF.
   c. During electrolysis of molten sodium chloride, calcium chloride and potassium fluoride are added.
8. The Haber process can be represented as follows



9. Why does the reaction
   $\geq C-Cl + MF \longrightarrow \geq C-F + MCl$
   proceed better with KF than with NaF?
10. Why lithium is kept wrapped in paraffin wax and not stored in kerosene oil?
11. Which alkali metal ion has maximum polarising power and why?
12. Why caesium can be used in photoelectric cell, while lithium cannot be?
13. Give reason for the decreasing order of the conductivity of the following.
    $Cs^{\oplus}_{(aq)} > Rb^{\oplus}_{(aq)} > K^{\oplus}_{(aq)} > Na^{\oplus}_{(aq)} > Li^{\oplus}_{(aq)}$
14. $NaHCO_3$ and NaOH cannot exist together in solution. Why?
15. On exposure to air, sodium hydroxide becomes liquid and after sometime it changes to white powder. Explain.
16. Alkali metals are obtained by the electrolysis of the molten salts and not by the electrolysis of their aqueous solutions. Give reason.
17. What happens when:
    a. Potassium metal is dropped in water
    b. Potassium is heated in free supply of air
    c. Potassium superoxide is dissolved in water
18. How sodium carbonate is manufactured by the Solvay process? State the principles involved.
19. a. Describe one method of manufacture of caustic soda.
    b. What happens when caustic soda reacts with
       i. Al metal ii. CO_2 iii. SiO_2
    c. Describe four industrial uses of caustic soda.
20. Answer the following:
    a. Which of the following has density greater than water? Li, Na, K, Cs.
    b. Arrange K, Li, Rb in order of increasing electrode potential.
    c. Arrange Na, Li, K and Cs in increasing order of metallic bond.
    d. Which among Na, K, Cs and Li forms stable hydride?
    e. On reacting with oxygen, potassium can form K_2O, KO_2 and K_2O_2. Is it correct?
    f. Give the name of the hardest alkali metal.
    g. Arrange the following in order of increasing polarising ability.
       $Li^{\oplus}, Na^{\oplus}, K^{\oplus}, Cs^{\oplus}$
    h. Mention some of the properties of alkali metals which increase down the group.

i. Mention some of the properties of alkali metals which decrease down the group.

21. Explain the following:
 a. Alkali metals are paramagnetic, but their salts are diamagnetic.
 b. The inside surface of a glass bottle containing caustic soda becomes dull.

22. Identify (A) and (B) in the following:

$$KO_2 + S \xrightarrow{\Delta} (A)$$
$$(A) + BaCl_2 \longrightarrow \underset{\text{White ppt.}}{(B)}$$

23. LiOH has been used by astronauts. Explain the use with the help of reaction.

24. Give the composition and action of baking powder.

25. Match the following:

	Column I		Column II
a.	Indian saltpetre	i.	NaCN
b.	Germicide	ii	$Na_2CO_3 \cdot 10H_2O$
c.	Chile saltpetre	iii.	$NaNO_3$
d.	Washing soda	iv	$NaHCO_3$
e.	Baking soda	v.	KNO_3
f.	Glauber's salt	vi.	$NaNH_4HPO_4 \cdot 4H_2O$
g.	Microcosmic salt	vii.	$(Na_2S_2O_3)$
h	Hypo salt	viii.	$Na_2SO_4 \cdot 10H_2O$

ANSWERS

20.
a. Li b. Li > Rb > K c. Li < Na < K < Rb
d. Li e. Yes f. Li
g. $Cs^{\oplus} < K^{\oplus} < Na^{\oplus} < Li^{\oplus}$

22. For (h) and (i), refer to Hints and Solutions.
$A \Rightarrow K_2SO_4$ $B \Rightarrow BaSO_4$

25. a. (v) b. (i) c. (iii)
d. (ii) e. (iv) f. (viii)
g. (vi) h. (vii)

Solved Examples

EXAMPLE 4.1

How many moles of CO_2 will be formed when a mixture containing 10 moles each of Li_2CO_3 and Na_2CO_3 are heated?

Sol. On heating, Li_2CO_3 decomposes to give Li_2O and CO_2, whereas K_2CO_3 do not decompose.

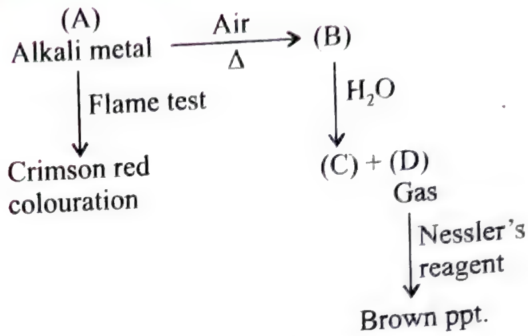
$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

Since one mole of Li_2CO_3 decomposes to give one mole of CO_2; 10 moles of CO_2 will be formed on heating a mixture containing 10 moles each of Li_2CO_3 and Na_2CO_3.

EXAMPLE 4.2

Alkali metal (A) on flame test gives a crimson red colour to the Bunsen flame. (A) on heating in air gives compound (C) and gas (D). Gas (D) with Nessler's reagent gives a brown precipitate. Identify (A), (B), (C) and (D).

Sol.



Flame colouration of (A) shows it to be lithium.

$$\underset{(A)}{Li} + \underset{(Air)}{O_2} \xrightarrow{\Delta} Li_2O$$

$$6Li + \underset{(Air)}{N_2} \xrightarrow{\Delta} 2Li_3N$$

$$Li_2O + H_2O \longrightarrow 2LiOH$$

$$\underset{(B)}{Li_3N} + H_2O \longrightarrow \underset{(C)}{LiOH} + \underset{(D)}{NH_3}$$

On hydrolysis of compound (B), the gas produced (D) gives a brown ppt. with Nessler's reagent, it shows the gas to be NH_3, which is produced only on the hydrolysis of Li_3N and not Li_2O. Hence, (B) is Li_3N.

Hence, (A) is Li; (B) is Li_3N; (C) is LiOH and (D) is NH_3.

EXAMPLE 4.3

Zinc on reaction with NaOH gives a salt (A) alongwith a gas (B). (A) on reaction with H_2S gas gives a white precipitate (C). Identify (A), (B) and (C).

Sol. $Zn + NaOH \longrightarrow \underset{(A)}{Na_2ZnO_2} + \underset{(B)}{H_2}$

$$Na_2ZnO_2 + H_2S \longrightarrow \underset{\substack{(C)\\ \text{Zinc sulphide}\\ \text{(white ppt.)}}}{ZnS\downarrow} + 2NaOH$$

Hence, (A) is Na_2ZnO_2 (sodium zincate), (B) is H_2 (hydrogen gas) and (C) is ZnS (zinc sulphide).

EXAMPLE 4.4

Identify (A), (B), (C) and (D) and give their chemical formulae.

$$(A) + NaOH \xrightarrow{\Delta} NaCl + NH_3 + H_2O$$
$$NH_3 + CO_2 + H_2O \longrightarrow (B)$$
$$(B) + NaCl \longrightarrow (C) + NH_4Cl$$
$$(C) \xrightarrow{\Delta} Na_2CO_3 + H_2O + (D)$$

Sol. $NH_4Cl + NaOH \xrightarrow{\Delta} NaCl + NH_3 + H_2O$
(A)

$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$
(B)

$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$
(B) (C)

$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$
(C) (D)

Hence, (A) is NH_4Cl, (B) is NH_4HCO_3, (C) is $NaHCO_3$ and (D) is CO_2.

EXAMPLE 4.5

A certain compound (A) is used in the laboratory for analysis, its aqueous solution gives the following reactions:

a. On addition to copper sulphate, a brown precipitate is obtained which turns white on addition of excess of the $Na_2S_2O_3$ solution.
b. On addition to the $Ag^{\oplus}$ ion solution, a yellow curdy precipitate is obtained which is insoluble in ammonium hydroxide.
Identify (A) and give equations for the reactions at steps (a) and (b).

Sol.

a. $\underset{\text{(aq. soln)}}{(A)} + CuSO_4 \longrightarrow \text{Brown ppt} \xrightarrow[\text{excess}]{Na_2S_2O_3} \text{white ppt.}$

b. $\underset{\text{(aq. soln)}}{(A)} + Ag^{\oplus}_{(soln)} \longrightarrow \underset{\text{Insoluble}}{\text{Yellow curdy ppt}} \xrightarrow{NH_4OH}$

(A) is KI

a. $KI_{(aq)} + CuSO_{4(aq)} \longrightarrow \underset{\text{white ppt.}}{Cu_2I_2} + K_2SO_4 + I_2$

$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$

b. $KI_{(aq)} + Ag^{\oplus}_{(soln)} \longrightarrow \underset{\text{Yellow curdy ppt}}{AgI\downarrow} + K^{\oplus}_{(aq)}$

AgI is insoluble in NH_4OH.

EXAMPLE 4.6

Identify (A), (B), (C) and (D) and give their formulae:

$(A)_{(aq)} + Zn \longrightarrow (B)_{(g)}$

$(A)_{(aq)} + (C) \xrightarrow{\Delta} PH_3$

$(A)_{(aq)} + NH_4Cl \longrightarrow (D)_{(g)}$

Compound (A) imparts golden yellow colour to the Bunsen flame.

Sol. Compound (A) imparts golden yellow colour to the Bunsen flame, it seems (A) is NaOH.

$\underset{(A)}{NaOH_{(aq)}} + Zn \longrightarrow Na_2ZnO_2 + \underset{(B)}{H_{2(g)}}$

$\underset{(A)}{NaOH_{(aq)}} + \underset{\substack{(C)\\\text{White phosphorous}}}{P_4} \xrightarrow{\Delta} NaH_2PO_2 + PH_3$

$\underset{(A)}{NaOH_{(aq)}} + NH_4Cl \longrightarrow NaCl + \underset{(D)}{NH_3\uparrow} + H_2O$

Hence, (A) is sodium (NaOH) hydroxide; (B) is hydrogen gas (H_2); (C) is white phosphorous (P_4) and (D) is ammonia gas (NH_3).

EXAMPLE 4.7

A certain compound (A) imparts a golden yellow flame and exhibits following reactions:

a. When a concentrated solution of (A) is boiled with Zn powder, hydrogen gas is evolved.
b. When an aqueous solution of (A) is added to an aqueous solution of stannous chloride, a white precipitate is obtained, which dissolves in excess of solution (A).

Identify (A) and give equations for the reactions in (i) and (ii).

Sol.

a. $\underset{(A)}{NaOH_{(aq)}} + Zn \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_{2(aq)}} + \underset{\text{Hydrogen gas}}{H_2\uparrow}$

b. $\underset{(A)}{NaOH_{(aq)}} + \underset{\text{Stannous chloride}}{SnCl_2} \longrightarrow \underset{\text{White ppt.}}{Sn(OH)_2\downarrow} + 2NaCl$

$Sn(OH)_2 + NaOH \longrightarrow \underset{\text{Soluble}}{Na_2SnO_2} + 2H_2O$

Hence, (A) is NaOH and imparts golden yellow colour to the flame.

EXAMPLE 4.8

An inorganic compound (A) loses its water of crystallisation on heating and its aqueous solution gives the following reactions:

a. It gives a white turbidity with dil HCl.
b. It decolourises a solution of iodine in KI.
c. It gives a white ppt. with $AgNO_3$ solution, which turns black on standing.

Sol. (A) is sodium thiosulphate, $Na_2S_2O_3{\cdot}5H_2O$.

a. $Na_2S_2O_3 + HCl \longrightarrow NaCl + H_2O + \underset{\text{White turbidity}}{S\downarrow} + SO_2$

b. $2Na_2S_2O_3 + \underset{(I_2 \text{ in KI})}{KI_3} \longrightarrow Na_2S_4O_6 + KI + 2NaI$

c. $Na_2S_2O_3 + 2AgNO_3 \longrightarrow \underset{\text{White ppt.}}{Ag_2S_2O_3\downarrow} + NaNO_3$

EXAMPLE 4.9

A white solid (A) is either Na_2O or Na_2O_2.

a. A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid.
b. Explain what would happen to the red litmus if the white solid were the other compound.

Sol.

a. Na_2O and Na_2O_2, when dissolved in water give

$Na_2O + H_2O \longrightarrow 2NaOH$

$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$

a. A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of compound (A), due to bleaching action of H_2O_2, thus compound (A) is Na_2O_2, i.e. sodium peroxide.

b. If white solid was Na_2O, the red litmus paper will turn blue due to the strong alkaline nature of the solution.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

EXAMPLE 4.10

a. When Cl_2 gas is bubbled through aqueous KOH, a firework explosive (A) is formed along with KCl and H_2O. Write down the balanced chemical reaction involved.

b. How many grams of (A) will be formed by 150 L of Cl_2, whose pressure is 980 mmHg at 25°C?

Sol.

a. When Cl_2 gas is bubbled through aqueous KOH, the following reaction takes place:

$$6KOH + 3Cl_2 \longrightarrow \underset{\text{Patassium chlorate}}{KClO_3} + 5KCl + 3H_2O$$

Firework explosive formed is potassium chlorate, $KClO_3$.

b. $PV = nRT$

where $P = \dfrac{980}{760}$ atm

$V = 150$ L

$n = ?$

$R = 0.0821$ L atm K^{-1} mol^{-1}

$T = 25°C = 25 + 273 = 298$ K

$$n = \frac{PV}{RT}$$

$$= \frac{980}{760} \times 150 \times \frac{1}{0.0821 \times 298}$$

$$= 7.906 \text{ moles}$$

Number of moles of $KClO_3$ produced $= \dfrac{1}{3} \times$ Number of moles of Cl_2

$$= \frac{1}{3} \times 7.906$$

$$= 2.635$$

Mass of $KClO_3$ formed $= 2.635 \times 122.5 = 322.79$ g

EXAMPLE 4.11

A binary salt of potassium (A) on heating with sulphur, compound (B) is formed. (B) on reacting with $BaCl_2$, gives a white precipitate (C) which is insoluble in concentrated HCl. Indentify (A), (B) and (C).

Sol. $(A) + S \xrightarrow{\Delta} (B)$

$$(A) + BaCl_2 \longrightarrow \underset{\text{White ppt.}}{(C)}$$

(A) is binary salt of potassium. (C) is white ppt. which is insoluble in conc HCl.

$$\underset{(A)}{2KO_2} + S \xrightarrow{\Delta} \underset{(B)}{K_2SO_4}$$

$$\underset{(B)}{K_2SO_4} + BaCl_2 \longrightarrow 2KCl + \underset{\substack{(C)\\ \text{White ppt}}}{BaSO_4\downarrow}$$

Hence, (A) is KO_2 (potassium peroxide); (B) is K_2SO_4 (potassium sulphate) and (C) is $BaSO_4$ (barium sulphate).

EXAMPLE 4.12

Identify from P to T.

a. $Na \xrightarrow{H_2O} P \xrightarrow{CO_2} Q \xrightarrow{SO_2} R \xrightarrow{Na_2S} S \xrightarrow{Ag^{\oplus}} T(\text{complex})$

b. What is the oxidation number of 'S' atom in compound S?

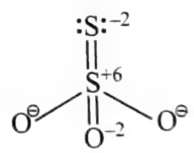
Sol.

a. $Na \xrightarrow{H_2O} \underset{(P)}{2NaOH} + CO_2 \longrightarrow \underset{(Q)}{Na_2CO_3} + H_2O$

$$\underset{(Q)}{Na_2CO_3} \xrightarrow{SO_2} \underset{(R)}{Na_2SO_3} + CO_2\uparrow$$

$$\underset{(T)}{Ag_2[S_2O_3]} \xleftarrow{2Ag^{\oplus}} \underset{(S)}{Na_2S_2O_3} \xleftarrow{Na_2S} \underset{(R)}{Na_2SO_3} + CO_2\uparrow$$

b. Structure of $S_2O_3^{2-}$:



Central S-atom is sp^3 hybridised and terminal S-atom is sp^2 hybridised hence more EN, hence its O.N is −2 and O.N. of central S-atom is +6.

EXAMPLE 4.13

$$Na_2O_2 \xrightarrow[0°C]{H_2O} A + B$$

$$Na_2O_2 \xrightarrow[\text{at } 25°C]{H_2O} A + C\uparrow + D.$$

Calculate the sum of bond order between same bonded atoms in B and C compounds.

Sol. $Na_2O_2 \xrightarrow[0°C]{H_2O} \underset{(A)}{NaOH} + \underset{(B)}{H_2O_2}$

$$Na_2O_2 \xrightarrow[\text{at } 25°C]{H_2O} \underset{(A)}{NaOH} + \underset{(B)}{O_2\uparrow} + \underset{(C)}{H_2O}$$

Bond order of (O–O) in $H_2O_2 = 1.0$

Bond order of (O–O) in $O_2 = 2.0$

Sum of bond order between same bonded atoms in B and C compounds $= 1 + 2 = 3.0$.

EXAMPLE 4.14

Identify metal (M), X, Y and Z.

Metal chloride (X) $\xrightarrow{Na_3[Co(NO_2)_6]}$ Yellow ppt. (Z)

Metal chloride (X) $\xrightarrow{HClO_4}$ White ppt. Soluble in H_2O insoluble in absolute alcohol.

Metal (M) is soft and silver white. It is oxidized by moist air and is covered with a blue film. $NH_4^{\oplus}$ ion also react with $Na_3[Co(NO_2)_6]$.

Sol. Reaction of metal (M) and $NH_4^{\oplus}$ ion with $[Co(NO_2)_6]$ ion, reveals that (M) should be potassium (K) and (X) is KCl

i. $\underset{(X)}{3KCl} + Na_3[Co(NO_2)_6] \longrightarrow \underset{\text{yellow ppt.}}{K_3[Co(NO_2)_6]} + 3NaCl$

This reaction is also given by $NH_4^{\oplus}$ ion.

ii. $\underset{(X)}{KCl} + HClO_4 \longrightarrow \underset{\substack{(Z) \\ \text{white ppt.}}}{KClO_4} + HCl$

Exercises

Single Correct Answer Type

Physical and Chemical Properties

1. Alkali metals do not exist in free state in nature because these are
   (1) Very reactive
   (2) Very volatile
   (3) Metallic in nature
   (4) Highly electronegative elements.
2. Alkali metals can be extracted from their salts by
   (1) Reduction with carbon
   (2) Electrolysis of aqueous solution of their halides
   (3) Electrolysis of fused halides
   (4) Reduction with aluminium
3. Which one of the alkali metal forms only, the normal oxide, M_2O?
   (1) Li (2) Na
   (3) K (4) Rb
4. The similarity in the properties of alkali metals is due to
   (1) Their same atomicity
   (2) Similar outer shell configuration
   (3) Same energy of outer shell
   (4) Same principal quantum number of outer shell
5. CsOH is
   (1) Strongly basic (2) Weakly basic
   (3) Slightly acidic (4) Amphoteric
6. $K^{\oplus}$ ion is isoelectronic with
   (1) $Na^{\oplus}$ (2) Ne
   (3) Ar (4) $Cs^{\oplus}$
7. Which of the following decomposes on heating?
   (1) LiOH (2) NaOH
   (3) KOH (4) CsOH
8. Among the alkali metals, the most abundant metal is
   (1) Na (2) K
   (3) Li (4) Cs
9. The alkali metal having the highest melting point is
   (1) Li (2) Na
   (3) Cs (4) Rb
10. Lithium forms
    (1) LiO (2) LiO_2
    (3) Li_2O (4) Li_2O_2
11. Which of the following metals is most commonly used in photochemical cells?
    (1) Lithium (2) Calcium
    (3) Caesium (4) Francium
12. The size of $Na^{\oplus}$ ion is same as that of
    (1) Ne atom (2) Na atom
    (3) K atom (4) None of these
13. Sodium can be extracted on a commercial scale by the electrolysis of fused sodium chloride. The process is called
    (1) Castner process (2) Down's process
    (3) Nelson process (4) Solvay process
14. Potassium is ________, ________ and ________ than sodium.
    (1) lighter, softer and more reactive
    (2) heavier, softer and less reactive
    (3) lighter, harder and more reactive
    (4) None of the above
15. Potassium can be prepared by
    (1) Heating K_2CO_3 with coke
    (2) Electrolysis of fused KOH
    (3) Heating KF with CaC_2
    (4) All the above
16. Which is an ore of potassium?
    (1) Carnallite (2) Cryolite
    (3) Dolomite (4) Bauxite
17. Which of the alkali metals have the highest density?
    (1) Cs (2) Li
    (3) Na (4) Rb
18. A sodium fire in the laboratory is extinguished by
    (1) Water (2) Petrol
    (3) Alcohol (4) CCl_4
19. The densities of Li, Na and K follow the order
    (1) $Li > Na < K$ (2) $Li < Na < K$
    (3) $Li < K < Na$ (4) $Li > Na > K$
20. The mobility of metal ions in aqueous medium ($Li^{\oplus}$, $Na^{\oplus}$, $K^{\oplus}$, $Rb^{\oplus}$) in the electric field, follows the order:
    (1) $Li^{\oplus} > Na^{\oplus} > K^{\oplus} > Rb^{\oplus}$ (2) $Rb^{\oplus} > Na^{\oplus} \equiv K^{\oplus} > Li^{\oplus}$
    (3) $Li^{\oplus} < Na^{\oplus} < K^{\oplus} < Rb^{\oplus}$ (4) $Na^{\oplus} \equiv K^{\oplus} > Rb^{\oplus} > Li^{\oplus}$
21. Which of the following elements combines directly with nitrogen to form its nitride?
    (1) Li (2) Na
    (3) K (4) Rb
22. Which of the following ion has the greatest polarising power?
    (1) $Li^{\oplus}$ (2) $K^{\oplus}$
    (3) $Na^{\oplus}$ (4) $Cs^{\oplus}$
23. Which of the following alkali metal carbonates decomposes easily by heat?
    (1) Li_2CO_3 (2) Na_2CO_3
    (3) K_2CO_3 (4) Cs_2CO_3
24. The metallic lustre of sodium is explained by the presence of
    (1) $Na^{\oplus}$ ions
    (2) The oscillation of loosely bound electrons
    (3) Loosely held electrons
    (4) *bcc* lattice

25. Which of the following is not a characteristic of alkali metals?

(1) Low IE
(2) Low EN
(3) Ions are isoelectronic with noble gases
(4) High EN

26. Among the alkali metals, the strongest reducing agent is

(1) Li (2) Na
(3) K (4) Rb

27. Potassium gives a ________ colour to the Bunsen flame.

(1) violet (2) blue
(3) apple green (4) brick red

28. Which of the following is strongly hydrated in aqueous solution?

(1) $Li^{\oplus}$ (2) $Na^{\oplus}$
(3) $K^{\oplus}$ (4) $Cs^{\oplus}$

29. Which of the following alkali metal does not form alum?

(1) Li (2) Na
(3) K (4) Rb

30. Sodium reacts with water more vigorously than lithium because

(1) It has high atomic mass
(2) It is more electronegative
(3) It is more electropositive
(4) It is a metal

31. Magnesium uranyl test is used for

(1) Sodium (2) Potassium
(3) Rubidium (4) Caesium

32. A solution of sodium metal in liquid ammonia is strongly reducing due to the presence of

(1) Sodium atom (2) Sodium hydride
(3) Sodium amide (4) Solvated electrons

33. On dissolving moderate amount of sodium metal in liquid NH_3 at low temperature, which one of the following does not occur?

(1) Blue-coloured solution is obtained.
(2) $Na^{\oplus}$ ions are formed in the solution.
(3) Liquid ammonia becomes a good conductor of electricity.
(4) Liquid ammonia remains diamagnetic.

34. The alkali metals form salt-like hydrides by the direct synthesis at elevated temperature. The thermal stability of these hydrides decreases in which of the following order?

(1) NaH > LiH > KH > RbH > CsH
(2) LiH > NaH > KH > RbH > CsH
(3) CsH > RbH > KH > NaH > LiH
(4) KH > NaH > LiH > CsH > RbH

35. What is the reaction occurring at the anode in Down's process for the extraction of sodium?

(1) $2Cl^{\ominus} \longrightarrow Cl_2 + 2e^{\ominus}$
(2) $4\overset{\ominus}{O}H \longrightarrow 2H_2O + O_2 + 4e^{\ominus}$
(3) $Na^{\oplus} + e^{\ominus} \longrightarrow Na$
(4) $NaOH \longrightarrow Na^{\oplus} + \overset{\ominus}{O}H$

36. Shine at freshly cut sodium is because of

(1) Oscillations of free electrons
(2) Weak metallic bonding
(3) Absorption of light in crystal lattice
(4) Presence of free valency at the surface

37. Among the alkali metals caesium is the most reactive because

(1) It has incomplete shell which is nearest to the nucleus
(2) It has a single electron in the valence shell
(3) It is the heaviest alkali metal
(4) The outermost electron is more loosely bound than the outermost electron of the other alkali metals

38. When sodium is added in scanty water, it catches fire. In this process which one of the following burns?

(1) Na (2) H_2O
(3) CO (4) H_2

39. Stable oxide is obtained by heating the carbonate of the elements

(1) Li (2) Na
(3) K (4) Rb

40. Ease with which hydrides are formed from Li to Cs:

(1) Decreases (2) Increases
(3) Remains the same (4) None of these

41. Prefix 'alkali' for alkali metals denotes:

(1) Silvery lustre (2) Metallic nature
(3) Active metals (4) Ashes of plants

42. In view of their low ionisation energies, the alkali metals are

(1) Weak oxidising agents (2) Strong reducing agents
(3) Strong oxidising agents (4) Weak reducing agents

43. Which of the following has the lowest melting point?

(1) Li (2) Na
(3) K (4) Cs

44. When sodium is treated with sufficient oxygen/air, the product obtained is

(1) NaO (2) Na_2O
(3) Na_2O_2 (4) NaO_2

45. Elements in the first column of the periodic table are called alkali metals. These metals have:

(1) A single valency electron
(2) One electron less than an inert gas configuration
(3) High melting points
(4) High ionisation potentials

46. When dry ammonia gas is passed over heated sodium (out of contact of air) the product formed is

(1) Sodium hydride (2) Sodium nitride
(3) Sodamide (4) Sodium cynamide

47. On dissolving moderate amount of sodium metal in liquid ammonia at low temperature, which of the following does not occur?

(1) Blue-coloured solution is obtained
(2) Ammoniated $Na^{\oplus}$ ions are formed in solution
(3) Liquid ammonia becomes good conductor of electricity
(4) The liquid ammonia remains diamagnetic

48. Which of the property of alkali metals is not listed correctly?
(1) The least electronegative metal: Cs
(2) A natural radioactive metal: Fr
(3) The alkali metal with the lowest density: K
(4) The most abundant alkali metal in the earth's crust: Na

49. Which one of the following statements is/are true for all the alkali metals?
(1) Their nitrates decompose on heating to give NO_2 and O_2.
(2) Their carbonates decompose on heating to give CO_2 and normal oxide.
(3) They react with halogens to give the halides of the type MX.
(4) They react with oxygen to give mainly the oxide, M_2O.

50. Which of the following metals is used for drying organic solvents?
(1) Magnesium (2) Sodium
(3) Platinum (4) Nickel

51. Which of the following does not illustrate the anomalous behaviour of lithium?
(1) Lithium reacts with nitrogen to form a nitride.
(2) Lithium is the hardest alkali metal.
(3) Lithium reacts with oxygen to form normal oxide only.
(4) Lithium carbonate decomposes on heating.

52. Pick out statement(s) which is/are not true about diagonal relationship of Li and Mg:
A Polarising powers of $Li^{\oplus}$ and Mg^{2+} ions are almost the same.
B Like Li, Mg decomposes water very fast.
C LiCl and $MgCl_2$ are deliquescent.
D Like Li, Mg readily reacts with liquid bromine at ordinary temperature.
(1) A and D (2) B and C
(3) Only B (4) B and D

53. Select incorrect statement
(1) Potassium is obtained by the electrolysis of fused KCl
(2) Al & Be shows diagonal relationship
(3) Na gives golden yellow colour and K gives violet colour in flame
(4) Potassium is prepared by reduction of molten KCl with Na at 850°C

Compounds of Alkali Metals

54. The formula of carnallite is
(1) $LiAl(Si_2O_5)_2$ (2) $KCl{\cdot}MgCl_2{\cdot}6H_2O$
(3) $K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$ (4) $KCl{\cdot}MgCl_2{\cdot}4H_2O$

55. Solvay process is used for the manufacture of
(1) Sodium metal (2) Washing soda
(3) Potassium chlorate (4) Ammonia

56. In Down's process, for manufacture of sodium metal, $CaCl_2$ is added to NaCl in order to
(1) Increase ionisation of NaCl
(2) Increase the melting point of NaCl
(3) Decrease the melting point of NaCl
(4) Increase conductance of electrolyte

57. The main process for the manufacture of sodium carbonate is
(1) Carbon process (2) Solvay process
(3) Down's process (4) Nelson process

58. Microcosmic salt is
(1) $Na(NH_4)\ HPO_4{\cdot}4H_2O$ (2) $Na(NH_4), H_2O$
(3) $Na(NH_3)HPO_4{\cdot}4H_2O$ (4) $K(NH_4)HPO_4{\cdot}2H_2O$

59. Which one is the highest melting halide?
(1) KCl (2) KBr
(3) KF (4) KI

60. Sodium thiosulphate, $Na_2S_2O_3{\cdot}5H_2O$ is used in photography to
(1) Reduce the AgBr grains to metallic Ag
(2) Convert metallic Ag to Ag salt
(3) Remove undecomposed AgBr as soluble silver thisoulphate complex
(4) Remove reduced silver

61. Baking soda is
(1) $Na_2CO_3{\cdot}10H_2O$ (2) $Na_2SO_4{\cdot}10H_2O$
(3) Na_2SO_4 (4) $NaHCO_3$

62. NaOH is manufactured by the electrolysis of brine in a specially designed cell called
(1) Castner–Kellner cell (2) Castner cell
(3) Solvay cell (4) Leblanc cell

63. Saltpetre is
(1) KNO_3 (2) $NaNO_3$
(3) NaCl (4) Na_2CO_3

64. Chile saltpetre is
(1) KNO_3 (2) $NaNO_3$
(3) Na_2SO_4 (4) $Na_2S_2O_3$

65. Glauber's salt is
(1) $Na_2CO_3{\cdot}10H_2O$ (2) $Na_2SO_4{\cdot}10H_2O$
(3) $FeSO_4{\cdot}7H_2O$ (4) $CuSO_4{\cdot}5H_2O$

66. Causticisation process is used for the preparation of
(1) Caustic soda (2) Caustic potash
(3) Slaked lime (4) Sodium carbonate

67. A neutral white sodium salt (A) on heating liberates a gas (B), leaving a highly alkaline residue (C). The gas (B) is colourless, odourless and turns lime water milky. (A) is
(1) $NaNO_3$ (2) $NaHCO_3$
(3) Na_2CO_3 (4) NaCl

68. A pair of substance which cannot exist together in solution is
(1) $NaHCO_3 + NaOH$ (2) $NaHCO_3 + Na_2CO_3$
(3) $Na_2CO_3 + NaOH$ (4) $NaOH + NaCl$

69. The product of electrolysis of an aqueous solution of K_2SO_4 using inert electrodes, at anode and cathode respectively are
(1) O_2 and H_2 (2) O_2 and K
(3) O_2 and SO_2 (4) O_2 and SO_3

70. When an aqueous solution of potassium ethanoate is electrolysed?
(1) Ethane and CO_2 gases are liberated at anode and H_2 gas at cathode.
(2) Ethane and CO_2 gases are liberated at cathode and H_2 gas at anode.
(3) Ethane and CO_2 gases are liberated at anode and K metal is deposited at cathode.
(4) Ethyne, H_2 and CO_2 are liberated at anode and K metal is deposited at cathode.

71. When Na_2CO_3 is added to an aqueous solution of $CuSO_4$
(1) $CuCO_3$ is precipitated
(2) Copper hydroxide is precipitated
(3) Basic copper carbonate is precipitated
(4) No reaction takes place

72. K_2CS_3 is called potassium ________.
(1) thiocarbide (2) thiocarbonate
(3) thiocyanate (4) sulphocyanide

73. 'Pearl ash' is
(1) K_2CO_3 (2) $KMnO_4$
(3) K_2O_3 (4) KOH

74. How many $Na^{\oplus}$ ions surround each $Cl^{\ominus}$ ion in NaCl crystal lattice?
(1) 4 (2) 6
(3) 8 (4) 12

75. Lithia water used for the treatment of gout is
(1) $LiHCO_3$ (2) Li_2CO_3
(3) Li_2SO_4 (4) LiOH

76. Lowig method is used for the preparation of
(1) KOH (2) NaOH
(3) Na_2CO_3 (4) $NaHCO_3$

77. KO_2 is used in oxygen cylinders in space and submarines because it
(1) Absorbs CO_2 and increases O_2 content
(2) Elminates moisture
(3) Absorbs CO_2
(4) Produces ozone

78. The stability of the following alkali metal chlorides follows the order:
(1) KCl > CsCl > NaCl > LiCl
(2) LiCl > KCl > NaCl > CsCl
(3) CsCl > KCl > NaCl > LiCl
(4) NaCl > KCl > LiCl > CsCl

79. The paramagnetic species is
(1) KO_2 (2) SiO_2
(3) TiO_2 (4) BaO_2

80. A fire extinguisher contains H_2SO_4 and
(1) $NaHCO_3$ and Na_2CO_3 (2) $NaHCO_3$ solution
(3) Na_2CO_3 (4) $CaCO_3$

81. Which of the following compound is used in gun powder?
(1) $LiNO_3$ (2) $NaNO_3$
(3) $Pb(NO_3)_2$ (4) KNO_3

82. Which of the following compounds is/are not soluble in water?
(1) Li_2CO_3 (2) LiF
(3) Li_3PO_4 (4) All of these

83. When a standard solution of NaOH is left in air for a few hours:
(1) A precipitate will form
(2) Strength will decrease
(3) Strength will increase
(4) The concentration of $Na^{\oplus}$ ions will remain constant

84. In the following sequence of reaction, identify the compounds (A), (B), (C) and (D):

$$\underset{\text{Solution}}{Na_2CO_3} \xrightarrow{SO_2} (A) \xrightarrow{Na_2CO_3} (B) \xrightarrow[\text{Heat}]{S} (C) \xrightarrow{AgNO_3} (D)$$

(1) Na_2SO_3, $NaHSO_3$, Na_2S, Ag_2S
(2) $NaHSO_3$, Na_2SO_3, $Na_2S_2O_3$, Ag_2S
(3) $NaHSO_3$, Na_2SO_4, Na_2S, Ag_2O
(4) Na_2SO_3, Na_2SO_4, $Na_2S_2O_3$, Ag

85. $ZnCl_2 + NaHCO_3 \xrightarrow{\text{Heat}} (A) \xrightarrow{\text{Heat}} (B) + (C) + H_2O$
$(B) + NaOH \longrightarrow (D)$
Identify the compound (D) present in the solution.
(1) $ZnCO_3$ (2) $Zn(OH)_2$
(3) ZnO (4) Na_2ZnO_2

86. The carbonate that will not decompose on heating is
(1) Na_2CO_3 (2) $CaCO_3$
(3) $SrCO_3$ (4) $BaCO_3$

87. Which one of the following electrolysis is used in Down's process of extracting sodium metal?
(1) NaCl + KCl + KF (2) NaCl
(3) NaOH + KCl + KF (4) NaCl + NaOH

88. The solubility of alkali metal hydroxides follows the order:
(1) LiOH < NaOH < KOH < RbOH < CsOH
(2) LiOH > NaOH > KOH> RbOH > CsOH
(3) LiOH > CsOH > RbOH > NaOH > KOH
(4) None of the above

89. The magnetic moment of KO_2 at room temperature is ________ BM.
(1) 1.41 (2) 1.73
(3) 2.23 (4) 2.64

90. Sodium peroxide which is a yellow solid, when exposed to air becomes white due to the formation of:
(1) H_2O_2 (2) Na_2O
(3) Na_2O and O_3 (4) NaOH and Na_2CO_3

91. Sodium hydride (NaH) when dissolved in water, produces
(1) Acidic solution (2) Basic solution
(3) Neutral solution (4) Cannot be predicted

92. The correct order of stability for the following superoxides is
(1) $KO_2 > RbO_2 > CsO_2$ (2) $RbO_2 > CsO_2 > KO_2$
(3) $CsO_2 > RbO_2 > KO_2$ (4) $KO_2 > CsO_2 > RbO_2$

93. For which one of the following minerals, the composition given is incorrect?
(1) Soda ash–(Na_2CO_3)
(2) Carnallite–($KCl \cdot MgCl_2 \cdot 6H_2O$)
(3) Borax–($Na_2B_4O_7 \cdot 7H_2O$)
(4) Glauber's salt–($Na_2SO_4 \cdot 10H_2O$)

94. In the case of alkali metals, the covalent character decreases in the order:
(1) MF > MCl > MBr > MI (2) MF > MCl > MI > MBr
(3) MI > MBr > MCl > MF (4) MCl > MI > MBr > MF

95. Which of the following oxides is not expected to react with sodium hydroxide?
(1) CaO (2) SiO_2
(3) BeO (4) B_2O_3

96. The reaction that takes place when Cl_2 gas is passed through conc NaOH solution is
(1) Oxidation (2) Reduction
(3) Displacement (4) Disproportionation

97. Among LiCl, RbCl, $BeCl_2$ and $MgCl_2$ the compound with the greatest and least ionic character respectively are
(1) LiCl, RbCl (2) RbCl, $BeCl_2$
(3) RbCl, $MgCl_2$ (4) $MgCl_2$, $BeCl_2$

98. Which of the following compounds on reaction with NaOH and H_2O_2 gives yellow colour?
(1) $Zn(OH)_2$ (2) $Cr(OH)_3$
(3) $Al(OH)_3$ (4) None of these

99. For the preparation of sodium thiosulphate by 'Spring's reaction', the reactants used are
(1) $Na_2S + Na_2SO_3 + Cl_2$ (2) $Na_2S + SO_2$
(3) $Na_2S + Na_2SO_3 + I_2$ (4) $Na_2SO_3 + S$

100. Li_2SO_4 is not isomorphous with sodium sulphate:
(1) Due to small size of lithium
(2) Due to high coordination number of lithium
(3) Due to high ionisation energy of lithium
(4) None of the above

101. The chloride that can be extracted with ether is
(1) NaCl (2) KCl
(3) LiCl (4) RbCl

102. Which of the following has the lowest melting point?
(1) NaCl (2) NaF
(3) NaBr (4) NaI

103. Oxone is
(1) CaO (2) N_2O
(3) Na_2O_2 (4) $NaBO_3$

104. One of the natural minerals of sodium is tincal. Its formula is
(1) $Na_2CO_3 \cdot 10H_2O$ (2) $NaNO_3$
(3) $Na_2B_4O_7 \cdot 10H_2O$ (4) NaCl

105. $Na_2CO_3 + Fe_2O_3 \longrightarrow A + CO_2$, what is A in the reaction?
(1) $NaFeO_2$ (2) Na_3FeO_3
(3) Fe_3O_4 (4) Na_2FeO_2

106. The principal products obtained on heating iodine with cold and concentrated caustic soda solution:
(1) NaIO + NaI (2) NaIO + $NaIO_3$
(3) $NaIO_3$ + NaI (4) $NaIO_4$ + NaI

107. Match the compounds given in (X) with uses in (Y),

(X)	(Y)
A. NaOH	1. Glass
B. $Na_2S_2O_3$	2. Germicide
C. NaCN	3. Antichlor
D. Na_2CO_3	4. Soap

Codes:

	A	B	C	D
(1)	4	3	2	1
(2)	3	4	1	2
(3)	2	3	4	1
(4)	1	2	3	4

108. The aqueous solutions of lithium salts are poor conductor of electricity rather than other alkali metals because of:
(1) high ionisation energy
(2) high electronegativity
(3) lower ability of $Li^{\oplus}$ ions to polarise water molecules
(4) higher degree of hydration of $Li^{\oplus}$ ions

109. $NaOH + CO \xrightarrow[5-10\text{ atm}]{200°C} A$. The product A is:
(1) $NaHCO_3$ (2) Na_2CO_3
(3) HCOONa (4) H_2CO_3

110. The electrolyte, used in Castner's process of sodium extraction is
(1) anhydrous Na_2CO_3 (2) aqueous NaOH
(3) NaCl + $CaCl_2$ (4) fused anhydrous NaOH

111. Based on lattice energy and other considerations, which one of the following alkali metal chloride is expected to have the highest melting point ?
(1) LiCl (2) NaCl
(3) KCl (4) RbCl

112. Which among the following is the least soluble in water
(1) NaF (2) LiF
(3) KF (4) RbF

113. The correct order of stability of hydrides of alkali metals is
(1) LiH > NaH > KH > RbH
(2) NaH > KH > RbH > LiH
(3) RbH > KH > NaH > LiH
(4) LiH > RbH > KH > NaH

114. The correct order of mobility of alkali metal ions in aqueous solution is

(1) $K^{\oplus} > Rb^{\oplus} > Na^{\oplus} > Li^{\oplus}$ (2) $Rb^{\oplus} > K^{\oplus} > Na^{\oplus} > LI^{\oplus}$

(3) $Li^{\oplus} > Na^{\oplus} > K^{\oplus} > Rb^{\oplus}$ (4) $Na^{\oplus} > K^{\oplus} > Rb^{\oplus} > Li^{\oplus}$

115. Select correct statement:

(1) Oxides (M_2O) and peroxides (M_2O_2) of alkali metals are diamagnetic and colourless.

(2) Superoxides (MO_2) of alkali metals are paramagnetic.

(3) Li and Na do not form superoxides.

(4) All are correct.

116. Which of the following salts does not form any precipitate with excess of NaOH?

(1) $ZnCl_2$ (2) $FeCl_3$

(3) $CrCl_3$ (4) $CuSO_4$

117. Which of the following is the best CO_2 absorber as well as source of O_2 in space capsule?

(1) KOH (2) K_2O_2

(3) KO_2 (4) LiOH

118. $X + H_2O \longrightarrow NaOH$

$\downarrow O_2, 400°C$

$Y \xrightarrow[\text{at } 25°C]{H_2O} NaOH + O_2$

Y is used in oxygenating in submarine. X and Y are:

(1) Na_2O_2 and O_2 (2) Na_2O_2 and Na_2O

(3) Na_2O and Na_2O_2 (4) Na_2O and O_2

119. $KO_2 + CO_2 + H_2O \xrightarrow[\text{Excess } CO_2]{} A + B$

Products A and B are, respectively

(1) $KHCO_3, O_2$ (2) K_2CO_3, O_2

(3) KOH, K_2CO_3 (4) $KHCO_3, H_2O$

120. $X + S \longrightarrow Y \xrightarrow{BaCl_2}$ white ppt.

X is paramagnetic in nature and contains 55% K. Thus X is

(1) K_2O_2 (2) K_2O

(3) K_2SO_4 (4) KO_2

121. What happens when a standard solution of NaOH is left in air for few hours?

(1) The strength of solution will increase

(2) The strength of solution will decrease

(3) A precipitate will form

(4) The concentration of $Na^{\oplus}$ ion in solution will remain same

122. $CaCl_2$ is preferred over NaCl for clearing ice on roads particularly in very cold countries. This is because.

(1) Eutectic mixture of $CaCl_2/H_2O$, freezes at $-55°C$ while that of $NaCl/H_2O$ freezes at $-18°C$.

(2) NaCl makes road slippery but $CaCl_2$ does not

(3) $CaCl_2$ is less soluble is H_2O than NaCl

(4) $CaCl_2$ is hygroscopic but NaCl is not

123. At high temperature Na reacts with Al_2O_3 to give a compound (A). Compound (A) reacts with solution of CO_2 gives compound B.

The compound (A) and (B) are, respectively

(1) Na_2O_2, $NaHCO_3$ (2) Na_2O, Na_2CO_3

(3) $NaAlO_2$, Na_2CO_3 (4) $NaAlO_2$, $NaHCO_3$

124. Aqueous solution of SO_2 reacts with excess of Na_2CO_3 to give compound (A) which on reaction with sulphur gives compound (B), compound (B) on reaction with $AgNO_3$ gives compound (C).

The compound (B) is:

(1) $NaHSO_3$ (2) Na_2SO_3

(3) $Na_2S_2O_3$ (4) $Na_2S_4O_6$

125. Select incorrect statements

(1) Baking soda is a mixture of (30% $NaHCO_3$ + 10% $Ca(H_2PO_4)_2$ + 40% starch + 20% $NaAl(SO_4)_2$)

(2) $Ca(H_2PO_4)_2$ is acidic and when moistened it reacts with $NaHCO_3$ giving CO_2

(3) $Pb(OH)_2$ on reaction with NaOH solution gives Na_2PbO_2

(4) Raw materials in solvay process are NH_4Cl and NaCl and by product in this process is $CaCl_2$

Multiple Correct Answers Type

Physical and Chemical Properties

1. Sulphides of which of the metals is/are soluble in water.

(1) Na (2) K

(3) Zn (4) Cu

2. Alkali metals are characterised by

(1) Good conductor of heat and electricity

(2) High oxidation potentials

(3) Low melting points

(4) Solubility in liquid ammonia

3. Select wrong statements about alkali metals:

(1) All form (MNH_2) amide

(2) All form superoxides (MO_2)

(3) All form ionic hydrides (MH)

(4) All form nitrides

4. A highly pure dilute solution of sodium in liquid ammonia:

(1) Shows blue colour

(2) Exhibits electrical conductivity

(3) Produces sodium amide

(4) Produces hydrogen gas

5. Li has the following abnormal behaviour in its group:

(1) Lithium carbonate decomposes into its oxide on heating, unlike other elements.

(2) LiCl is covalent in nature.

(3) Li_3N is a stable compound.

(4) LiCl is a poor conductor of electricity in molten state.

6. Which among the following compounds is paramagnetic?

(1) KO_2 (2) K_2O_2

(3) K_2O (4) NO_2

7. Nitrate of which of the following elements are converted to their oxides on heating?

(1) Li (2) Na

(3) K (4) Mg

8. The compound(s) formed upon combustion of sodium metal in excess air is/are
(1) Na_2O_2 (2) Na_2O
(3) NaO_2 (4) NaOH

9. An alloy of Na and K is
(1) Liquid at room temperature
(2) Used in specially designed thermometers
(3) Unstable
(4) Solid at room temperature

10. Sodium metal can be kept under
(1) Kerosene (2) Benzene
(3) Toluene (4) Alcohol

11. Sodium metal cannot be stored under
(1) Kerosene (2) Toluene
(3) Alcohol (4) Water

12. An element having electronic configuration $[Rn]6s^1$ will:
(1) Form basic oxide
(2) Can be used in photoelectric cell
(3) Form acidic oxide
(4) Has high ionisation enthalpy

13. Which of the following compound(s) will impart a golden yellow colour to the Bunsen flame?
(1) KCl (2) K_2CO_3
(3) NaCl (4) Na_2CO_3

14. Which of the following compound(s) is/are paramagnetic.
(1) KO_2 (2) RbO_2
(3) TiO_2 (4) SiO_2

15. Identify the correct statement:
(1) Elemental sodium is easily oxidised.
(2) Elemental sodium is soluble in ammonia.
(3) Elemental sodium is a strong oxidising agent.
(4) Elemental sodium can be prepared and isolated by electrolysing an aqueous solution of sodium chloride.

16. Select the incorrect statements.
(1) Lithium reacts with nitrogen to form nitrides.
(2) Potassium is the most abundant alkali metal in the earth's crust.
(3) Lithium is the least electronegative alkali metal.
(4) Na and K form complexes.

17. Consider the following statements and select the correct answer.
Ammoniated solution of alkali metals are reducing agent due to presence of free ammoniated or solvated electrons. That can reduce
(1) O_2 to O_2^{2-}
(2) Non terminal alkyne
(3) Aromatic ring
(4) $[Ni(CN)_4]^{2-}$ to $[Ni(CN)_4]^{4-}$

18. Which of the following statement about alkali metals in liquid NH_3 is/are incorrect.
(1) The solution have strong oxidizing properties.
(2) Charge transfer is responsible for the colour of the solution.
(3) Both the dilute and concentrated solution are equally paramagnetic in nature.
(4) With concentrated liquid NH_3, solvated e^-'s associate to form electron-pairs and paramagnetic character decreases.

19. Select the incorrect statements.
(1) Potassium on burning in moist air give smell of NH_3
(2) Sodium can be prepared by electrolyzing fused NaCl
(3) The metallic lusture of alkali metals is due to diffusion of their ions
(4) The dilute solution of alkali metals in NH_3 are bronze coloured which changes to blue with increasing concentration.

20. Select the correct statements
(1) Potassium metal is commercially prepared by the reduction of molten KCN with Na because Na prefers to bind $Cl^{\ominus}$ ion in preference to $K^{\oplus}$ ions
(2) The aqueous solution of Li salts are poor conductor of electricity rather than other alkali metals because of lower ability of $Li^{\oplus}$ ions to polarize water molecule
(3) Potassium sesquoxide (K_2O_3) is prepared by thermal decomposition of KO_2. K_2O_3 contains K_2O_2 and KO_2 in 1:1 ratio is paramagnetic
(4) Out of KO_2 and KO_3, KO_2 is paramagnetic

Compounds of Alkali Metals

21. During electrolysis of aqueous solution of NaCl in Castner Kellner cell, the gas(es) produced are
(1) Cl_2 (2) O_2
(3) H_2 (4) HCl

22. Which of the following compounds decompose on heating?
(1) CsOH (2) KOH
(3) $LiNO_3$ (4) $NaHCO_3$

23. Which of the following compounds is/are not soluble in water?
(1) NaCl (2) LiF
(3) Li_2CO_3 (4) Na_2CO_3

24. Carnallite is an ore of
(1) Sodium (2) Potassium
(3) Magnesium (4) Aluminum

25. Which of the following compound is/are efflorescent?
(1) Washing soda (2) Caustic soda
(3) Caustic potash (4) Epsom salt

26. KO_2 finds use in breathing equipment and safeguards the user to breathe in oxygen generated internally in the apparatus without being exposed to toxic fumes outside. The supply of oxygen is due to
(1) Slow decomposition of KO_2
(2) Reaction of KO_2 with CO_2 in the exhaled air
(3) Reaction of KO_2 with moisture in the essential air
(4) Fast decomposition of KO_2

27. Brine solution on electrolysis will give
(1) NaOH (2) Cl_2
(3) O_2 (4) H_2

28. Which of the following reaction(s) is/are correct?
(1) $\underset{\text{(Hot and conc soln)}}{Cl_2 + NaOH} \longrightarrow NaCl + NaClO_3 + H_2O$
(2) $P_4 + NaOH + H_2O \longrightarrow NaH_2PO_2 + PH_3$
(3) $S + NaOH \xrightarrow{\Delta} Na_2S_2O_3 + Na_2S + H_2O$
(4) $C + NaOH \xrightarrow{\Delta} Na_2SiO_3 + H_2$

29. When a mixture of Li_2CO_3 and $Na_2CO_3{\cdot}10H_2O$ is heated strongly, there occurs a loss of mass due to
(1) Decomposition of Li_2CO_3
(2) Loss of water by $Na_2CO_3{\cdot}10H_2O$
(3) Decomposition of $Na_2CO_3{\cdot}10H_2O$
(4) None of the above

30. The pairs of compounds which cannot exist together in aqueous solution are
(1) NaH_2PO_4 and Na_2HPO_4 (2) Na_2CO_3 and $NaHCO_3$
(3) NaOH and NaH_2PO_4 (4) $NaHCO_3$ and NaOH

31. Which of the following is/are correct?
(1) Sodium thiosulphate is called hypo.
(2) Sodium peroxide is called oxone.
(3) Potassium carbonate is called pearl ash.
(4) Sodium nitrate is called Indian nitre.

32. Sodium chloride is known as
(1) Table salt (2) Common salt
(3) Soda ash (4) Rock salt

33. The compounds used in Solvay process are
(1) Na_2SO_4 (2) NaCl
(3) NH_3 (4) $CaCO_3$

34. Which of the following carbonates does not evolve CO_2 on heating?
(1) Li_2CO_3 (2) $MgCO_3$
(3) Na_2CO_3 (4) K_2CO_3

35. Select the correct statement:
(1) Lithium carbonate is insoluble in water.
(2) Potassium carbonate is soluble in water.
(3) Barium carbonate is soluble in water.
(4) Lithium bicarbonate is insoluble in water.

36. Which of the follwing is/are found in the solid state?
(1) $LiHCO_3$ (2) $KHCO_3$
(3) $NaHCO_3$ (4) NH_4HCO_3

37. Nitrogen dioxide cannot be obtained by heating
(1) KNO_3 (2) $NaNO_3$
(3) $AgNO_3$ (4) $Cu(NO_3)_2$

38. The hydroxide of which metal ion(s) is/are soluble in excess of NaOH solution
(1) Al^{3+} (2) Zn^{2+}
(3) Fe^{3+} (4) Cu^{2+}

39. Pick out the statement(s) which is/are not true about the diagonal relationship of Li and Mg.
(1) LiCl and $MgCl_2$ are deliquescent.
(2) Like Li, Mg decomposes water very fast.
(3) Polarising powers of $Li^{\oplus}$ and Mg^{2+} are almost the same.
(4) Like Li, Mg readily reacts with liquid ammonia at ordinary temperature.

40. Select the correct statements.
(1) Oxides and peroxides of alkali metals are diamagnetic and colourless.
(2) Superoxides of alkali metals are paramagnetic.
(3) LiCl and $MgCl_2$ are deliquescent.
(4) Melting point and boiling point of alkali metals increases from Li to Cs.

41. Select the correct statements.
(1) Amongst alkali metal perchlorates, $LiClO_4$ is most soluble in H_2O.
(2) Amongst alkali metal carbonates, Cs_2CO_3 has highest thermal stability.
(3) K when heated strongly in oxygen it forms K_2O.
(4) Amongst, Li_2CO_3, LiOH and $LiNO_3$, oxygen is liberated by $LiNO_3$ on heating.

42. Select correct statements.
(1) Sodium peroxide (Na_2O_2) is used to purify the air in submarine because it reacts with O_2 to form sodium superoxide
(2) Amongst alkali metal chlorides, LiCl has lowest melting point
(3) Amongst alkali metal fluorides, LiF is least soluble in H_2O
(4) $Na_2CO_3.NaHCO_3.2H_2O$ is a mineral called trona

43. Select the correct solubilities in water.
(1) KF > NaF > LiF
(2) $KNO_3 > NaNO_3 > LiNO_3$
(3) $K_2CO_3 > Na_2CO_3 > Li_2CO_3$
(4) LiF > NaF > KF

44. Which of the following gives $NO_2(g)$ on heating.
(1) $NaNO_3$ (2) $Hg(NO_3)_2$
(3) $AgNO_3$ (4) $Cu(NO_3)_2$

45. Select the correct statements.
(1) Oxide ion, peroxide ion and superoxide ions are related to each other as follows:

$$\underset{\text{Oxide ion}}{O^{2-}} \xrightarrow{\frac{1}{2}O_2} \underset{\text{Peroxide ion}}{O_2^{2-}} \xrightarrow{O_2} \underset{\text{Superoxide ion}}{2O_2^-}$$

(2) O_2^{2-} and O_2^- are stable towards water
(3) KO_2 will liberate O_2 when reacts with ice cold water
(4) Alkali metal oxides, peroxides and superoxides acts as bronsted acid

46. Select the incorrect statements.
(1) K_2CO_3 can be prepared by solvay process
(2) An aqueous solution of I_2 becomes colourless on adding excess of NaOH solution.

(3) On exposure to air, NaOH becomes liquid and after sometimes it changes to yellow powder.

(4) NaCl is hygroscopic and table salt on exposure to air damps up.

17. Select the correct statements.

(1) Na_2O_2 is powerful oxidant and bleaches red litmus paper to white in aqueous solution

(2) NaOH solution reacts with Zn powder and H_2 gas is liberated

(3) NaOH solution reacts with aqueous solution of $SnCl_2$, black ppt. is formed which is soluble in excess of NaOH

(4) Bottles containing NaOH solution is not closed by glass cork

Linked Comprehension Type

Paragraph 1

The first element of a group differs from its congeners, i.e. other members of the group in many ways. These differences may be due to the following:

i. Small size of atom and ion.

ii. High electronegativity.

iii. Non-availability of low lying *d*-orbitals.

The first element of a group shows resemblance with the second element of the adjacent group on the right. This is known as diagonal relationship.

1. Metal (M) + $N_2 \longrightarrow$ Nitride $\xrightarrow[\text{Hydrolysis}]{H_2O}$ NH_3

Metal (M) can be

(1) Li (2) Na

(3) K (4) Mg

2. Lithium exhibits many physical and chemical similarities with magnesium. The reason is:

(1) Both have the same size.

(2) Both are found in native state.

(3) Both have the same ionisation enthalpies.

(4) Both have the same electronic configuration.

3. In dry air, lithium and sodium react to give

(1) Li_2O, Li_3N, Na_2O

(2) Li_2O, Na_2O

(3) Li_2O, Li_3N, NH_3, Na_2O

(4) Li_2O, Li_3N, Na_2O, Na_3N

4. On heating, which of the following gives NO_2?

(1) $NaNO_3$ (2) $LiNO_3$

(3) NH_4NO_3 (4) NH_4NO_2

5. Which of the following is a false statement?

(1) Lithium has greater hardness as compared to other alkali metals.

(2) $LiHCO_3$ and $Mg(HCO_3)_2$ do not exist in the solid state.

(3) Lithium and magnesium form nitrides on reacting with nitrogen but other alkali metals do not.

(4) Alkali metal fluorides are highly soluble in water.

Paragraph 2

On exposure to air, alkali metals get tarnished due to formation of oxides, hydroxides and carbonates on their surface. When heated in air or oxygen they burn vigorously forming different types of oxides depending upon the nature of the metal.

The formation and stability of these metals can be explained on the basis of size of alkali metal ion and the anion. Peroxides are colourless, while superoxides are coloured. The normal oxides are basic while peroxides and superoxides act as oxidising agents.

6. Among NaO_2, Na_2O_2, Li_2O, CsO_2 unpaired electron is present in

(1) Na_2O_2 and Li_2O (2) Na_2O_2

(3) Li_2O (4) CsO_2 and NaO_2

7. On heating in excess of oxygen, lithium gives

(1) Li_2O (2) LiO

(3) Li_2O_2 (4) LiO_2

8. Oxone is

(1) Li_2O (2) Na_2O_2

(3) KO_2 (4) CsO_2

9. On heating in excess of oxygen, potassium gives

(1) K_2O (2) KO

(3) K_2O_2 (4) KO_2

10. Na_2O_2 has light yellow colour. This is due to

(1) Presence of traces of NaO_2.

(2) Presence of unpaired electron in the molecule.

(3) Presence of traces of Na_2O.

(4) None of the above.

Paragraph 3

Alkali metal salts are ionic and soluble in water. The solubility of an ionic compound depends on (i) lattice enthalpy and (ii) hydration enthalpy.

These two factors oppose each other. If hydration enthalpy is high, the ions will have greater tendency to be hydrated and therefore the solubility will be high. The smaller the cation, the greater is the degree of hydration. The reducing behaviour of alkali metals in solution is also dependent on the hydration enthalpy besides other factors.

11. The radius of which of the hydrated ion is the highest?

(1) $Li^{\oplus}_{(aq)}$ (2) $Na^{\oplus}_{(aq)}$

(3) $K^{\oplus}_{(aq)}$ (4) $Rb^{\oplus}_{(aq)}$

12. The hydration energy is maxium for

(1) $Li^{\oplus}$ (2) $Na^{\oplus}$

(3) $K^{\oplus}$ (4) $Rb^{\oplus}$

13. The ionic mobility of $Li^{\oplus}$ is less than that of the $Na^{\oplus}$ ion in solution because

(1) $Li^{\oplus}$ ion has a high charge density.

(2) $Li^{\oplus}$ ion has the highest hydration tendency.

(3) $Li^{\oplus}$ ion has the highest ionisation enthalpy.

(4) $Li^{\oplus}$ ion has two electrons.

14. Which of the following is the strongest reducing agent

(1) Li (2) Na

(3) K (4) Rb

Paragraph 4

In the manufacture of sodium carbonate, following reactions are involved:

$$(A) \xrightarrow{\Delta} (B) + CO_2$$

$$(B) + H_2O \longrightarrow (C) \xrightarrow{+NH_4Cl} (D) \xrightarrow{+H_2O} \underset{\text{Solution}}{(E)}$$

$$(E) + CO_2 \longrightarrow (F)$$

$$(F) + NaCl \longrightarrow (G) \xrightarrow{\text{Heat}} Na_2CO_3 + CO_2 + H_2O$$

(D) is a gas which is soluble in H_2O

15. The name of the process is
(1) Solvay (2) Salt cake
(3) Lowig (4) Gossage

16. (A) is
(1) $Ca(HCO_3)_2$ (2) $CaCO_3$
(3) CaC_2 (4) $NaHCO_3$

17. (B) is
(1) CaO (2) Ca_2O_2
(3) CaO_2 (4) Na_2O

18. (C) is
(1) Calcium hydroxide (2) Sodium hydroxide
(3) Calcium oxide (4) None of these

19. (E) and (F) are
(1) NH_4OH and NH_4HCO_3 (2) NaOH and $NaHCO_3$
(3) $Ca(OH)_2$ and $Ca(HCO_3)_2$ (4) None of these

20. (G) is $NaHCO_3$. The other compound formed with (G) is
(1) NH_4Cl (2) NH_4OH
(3) $CaCl_2$ (4) None of these

Matrix Match Type

This section contains questions each with two coloumns I and II. Match the items given in column I with that in column II.

1.

	Column I		Column II
a.	Carnallite	i.	$SrCO_3$
b.	Celestine	ii.	$Na_2SO_4 \cdot 10H_2O$
c.	Strontianite	iii.	NaCl
d.	Glauber's salt	iv.	$KCl.MgCl_2 \cdot 6H_2O$
e.	Spodumene	v.	$SrSO_4$
f.	Slyvite	iv.	$Li\,AlSi_2O_6$

2.

	Column I		Column II
a.	Chile salt petre	i.	Used in photoelectric cells
b.	Baking soda	ii.	KOH
c.	Caustic soda	iii.	$NaHCO_3$
d.	Caustic potash	iv.	$Na_2CO_3 \cdot 10H_2O$
e.	Washing soda	v.	$NaNO_3$
f.	Caesium	vi.	NaOH

3.

	Column I		Column II
a.	Metal used in photoelectric cell	i.	$Na_2SO_4 \cdot 10H_2O$
b.	Radioactive element	ii.	$Na\,AlSi_3O_5$
c.	Deliquescent	iii.	Francium
d.	Efflorescent	iv.	NaOH
e.	Glauber's salt	v.	Caesium
f.	Albite	vi.	$Na_2CO_3 \cdot 10H_2O$

4.

	Column I		Column II
a.	Gives CO_2 on heating	i.	Na
b.	Pink-violet flame colouration	ii.	Cs
c.	Forms superoxide on heating with O_2	iii.	K_2CO_3
d.	Used in photoelectric cells	iv.	$NaHCO_3$
e.	Form monoxide on heating with oxygen	v.	K
f.	Forms peroxide on heating with oxygen	vi.	Li

5. Match the items given in Column I with that in Column II and III

	Column I		Column II		Column III
	Alkali metals		Characteristics (I)		Characteristics (II)
a.	Li	i.	Highest electrical conductivity or ionic mobility at infinite dilution	p.	Photo-electric effect
b.	Na	ii.	Concentration of alkali metal ion is $(5 \times 10^{-3}$ to $10 \times 10^{-3})$M in RBC	q.	Crimson red in flame
c.	K	iii.	Down's cell	r.	Highest radii of hydrated ion
d.	Cs	iv.	Forms the most stable nitrides among the alkali metals	s.	Sylvine
				t.	Solvay ammonia process

For Q.6 to Q.9
Answer the questions given below by appropriately matching the information given in three column of the following table.

Column I E.C. of 1^{st} group elements		Column II Characteristics (I)		Column III Characteristics (II)
a. $4s^1$	i.	Carbonates of alkali metal on heating gives: oxides + CO_2	p.	Sulphates of alkali metal do not form alum.
b. $6s^1$	ii.	With excers of O_2, on heating alkali metal forms superoxides	q.	Violet in flame colouration
c. $2s^1$	iii.	Nitrates of alkali metal on heating gives: Oxides + $NO_2 + O_2$	r.	Least reducing character
d. $3s^1$	iv.	Nitrates of alkali metal on heating gives: Nitrites + O_2	s.	With excers of O_2, on heating alkali metal forms peroxides
			t.	Blue in flame colouration

6. For caesium, correct combination is:
(1) b–ii–t (2) b–ii, iv–t
(3) b–iv–t (4) b–ii, iv–q

7. For lithium, correct combination is:
(1) c–i, iii–s (2) c–i–p
(3) c–iii–p (4) c–i, iii–p

8. For potassium, correct combination is:
(1) a–ii, iv–q (2) a–ii–q
(3) a–iv–q (4) a–iii–q

9. For sodium, correct combination is:
(1) d–iv–r (2) d–iv–s
(3) d–iv–r, s (4) b–ii–r,s

Numerical Value Type

1. What is the relative abundance of soldium by weight in the earth's crust?
2. Trona is a natural hydrated mixed compound of sodium found in nature. In one molecule, how many sodium bicarbonate molecules are present?
3. Washing soda on standing in air effloresces. How many water molecules are lost?
4. Copper sulphate reacts with NaCN to form a cyanide complex. Write the balanced equation and find the number of NaCN molecules involved in the equation for one mole of $CuSO_4$.
5. Calculate heat of solution of NaCl from the following data:
Hydration energy of $Na^{\oplus} = -389$ kJ mol^{-1}
Hydration energy of $Cl^{\ominus} = -382$ kJ mol^{-1}
Lattice energy of NaCl $= -776$ kJ mol^{-1}
6. Potassium iodide reacts with acidified $K_2Cr_2O_7$. How many moles of KI are required for one mole of $K_2Cr_2O_7$?
7. On heating 8 moles each of Li_2CO_3 and K_2CO_3, how many moles of CO_2 evolved?
8. How many alkali metals are known?
9. How many water molecules are associated with washing soda?
10. How many moles of ammonia are produced, on hydrolysis of five moles of Li_3N?

Archives

JEE Main

Single Correct Answer Type

1. The main oxides formed on combustion of Li, Na and K in excess of air are respectively:
(1) Li_2O, Na_2O_2 and KO_2 (2) Li_2O, Na_2O and KO_2
(3) Li_2O_2, Na_2O_2 and K_2O (4) Li_2O_2, Na_2O_2 and KO_2
(JEE Main 2016)

JEE Advanced

Single Correct Answer Type

1. An aqueous solution of $Na_2S_2O_3$ on reaction with Cl_2 gives
(1) $Na_2S_4O_6$ (2) $NaHSO_4$
(3) NaCl (4) NaOH
(IIT-JEE 2008)

Multiple Correct Answers Type

1. The compound(s) formed upon combustion of sodium metal in excess air is/are
(1) Na_2O_2 (2) Na_2O
(3) NaO_2 (4) NaOH
(IIT-JEE 2009)

2. The pair(s) of reagents that yield paramagnetic species is/are
(1) Na and excess of NH_3 (2) K and excess of O_2
(3) Cu and dilute HNO_3 (4) O_2 and 2-ethylanthraquinol
(JEE Advanced 2014)

Answers Key

EXERCISES

Single Correct Answer Type

1. (1)	2. (3)	3. (1)	4. (2)	5. (1)
6. (3)	7. (1)	8. (1)	9. (1)	10. (3)
11. (3)	12. (4)	13. (2)	14. (1)	15. (4)
16. (1)	17. (1)	18. (4)	19. (3)	20. (3)
21. (1)	22. (1)	23. (1)	24. (2)	25. (4)
26. (1)	27. (1)	28. (1)	29. (1)	30. (3)
31. (1)	32. (4)	33. (3)	34. (2)	35. (1)
36. (1)	37. (4)	38. (4)	39. (1)	40. (1)
41. (4)	42. (2)	43. (4)	44. (3)	45. (1)
46. (3)	47. (4)	48. (3)	49. (1, 3)	50. (2)
51. (2)	52. (4)	53. (1)	54. (2)	55. (2)
56. (3)	57. (2)	58. (1)	59. (3)	60. (3)
61. (4)	62. (1)	63. (1)	64. (2)	65. (2)
66. (1)	67. (2)	68. (1)	69. (1)	70. (1)
71. (3)	72. (2)	73. (1)	74. (2)	75. (1)
76. (2)	77. (1)	78. (1)	79. (1)	80. (1)
81. (4)	82. (4)	83. (2)	84. (2)	85. (4)
86. (1)	87. (1)	88. (1)	89. (2)	90. (4)
91. (2)	92. (3)	93. (3)	94. (3)	95. (1)
96. (4)	97. (2)	98. (2)	99. (3)	100. (1)
101. (3)	102. (4)	103. (3)	104. (3)	105. (1)
106. (1)	107. (1)	108. (4)	109. (3)	110. (4)
111. (2)	112. (2)	113. (1)	114. (2)	115. (4)
116. (1)	117. (3)	118. (3)	119. (1)	120. (4)
121. (2)	122. (1)	123. (2)	124. (3)	125. (4)

Multiple Correct Answers Type

1. (1, 2)	2. (1, 2, 4)	3. (2, 4)
4. (1, 2)	5. (1, 2, 3)	6. (1, 4)
7. (1, 4)	8. (1, 2)	9. (2)
10. (1, 2, 3)	11. (3, 4)	12. (1, 2)
13. (3, 4)	14. (1, 2)	15. (1, 2)
16. (2, 3, 4)	17. (1, 2, 3, 4)	18. (1, 2, 3)
19. (1, 2, 3, 4)	20. (1, 2)	21. (1, 3)
22. (3, 4)	23. (2, 3)	24. (2, 3)
25. (1, 4)	26. (2, 3)	27. (2, 3, 4)
28. (1, 2, 3)	29. (1, 2)	30. (3, 4)
31. (1, 2, 3)	32. (1, 2, 4)	33. (2, 3, 4)
34. (3, 4)	35. (1, 2)	36. (2, 3, 4)
37. (1, 2)	38. (1, 2)	39. (2, 4)
40. (1, 2, 3)	41. (1, 2, 4)	42. (2, 3, 4)
43. (1, 2, 3)	44. (2, 3, 4)	45. (1, 3)
46. (1, 3, 4)	47. (1, 2, 4)	

Linked Comprehension Type

1. (1, 4)	2. (1)	3. (1)	4. (2)	5. (4)
6. (4)	7. (1)	8. (2)	9. (3)	10. (2)
11. (1)	12. (1)	13. (1, 2)	14. (1)	15. (1)
16. (2)	17. (1)	18. (1)	19. (1)	20. (1)

Matrix Match Type

Q. No.	a	b	c	d	e	f
1.	iv	v	i	ii	vi	iii
2.	v	iii	vi	ii	iv	i
3.	v	iii	iv	vi	i	ii
4.	iv	iii	ii	ii	vi	i, v
5.	iv–q.r	iii–t	ii–s	i–p		

6. (4) 7. (4) 8. (1) 9. (3)

Numerical Value Type

1. (7)	2. (1)	3. (9)	4. (5)	5. (5)
6. (6)	7. (8)	8. (6)	9. (10)	10. (5)

ARCHIVES

JEE Main

Single Correct Answer Type

1. (1)

JEE Advanced

Single Correct Answer Type

1. (2)

Multiple Correct Answers Type

1. (1, 2) 2. (1, 2, 3)

5 s-Block Group 2 Elements Alkaline Earth Metals

OVERVIEW

Group 2: Alkaline Earth Metals

1. General electronic configuration: ns^2.
2. Like alkali metals, the alkaline earth metals are also highly reactive and hence do not occur in the free state but widely distributed in nature in the combined state as silicates, sulphates, phosphates and carbonates.
3. They are called alkaline earth metals because they also dissolve in water and produce alkaline solution. Their oxides are found in earth's crust and are very stable to heat and fire. They have metallic properties.
4. Ca is the 5th, Mg is the 6th, Ba is the 14th, Sr is the 15th and Be is the 51st most abundant elements by weight in the earth's crust.
5. Be is found in small quantities as silicate minerals beryl, $Be_3Al_2Si_6O_8$ and phenacite, Be_2SiO_4.
6. Mg occurs approximately 0.14% in sea water as chlorides and sulphates. Mg occurs as magnesite $MgCO_3$, dolomite $CaMg(CO_3)_2$, epsomite $MgSO_4 \cdot 7H_2O$ and carnallite $(KCl)_2MgCl_2 \cdot 6H_2O$ or $K_2MgCl_4 \cdot 6H_2O$ and langbeinite $K_2Mg_2(SO_4)_3$ deposits.
7. Ca occurs as $CaCO_3$ in the form of limestone, marble and chalk.

   Important minerals of Mg are gypsum ($CaSO_4 \cdot 2H_2O$) and fluoroptite $[3(Ca_3(PO_4)_2 \cdot CaF_2]$.
8. The minerals of Sr are strontianite ($SrCO_3$) and celestite ($SrSO_4$).
9. **Flame colouration**

Metal	Be	Mg	Ca	Sr	Ba
Colour	—	—	Brick red	Crimson	Apple green

   Be and Mg do not impart flame colour because their IE's are very high and their outermost electrons are not excited by flame.
10. The general relationship throughout the group is similar to that in group 1.
11. IE_1 of group 2 > IE_1 of group 1. (Due to smaller size and higher Z_{eff} than those of group 1.)

    But IE_2 of group 2 < IE_2 of group 1 (removal of second electron in group 2 requires much less energy than that in the case of group 1).
12. They exist in M^{2+} oxidation state.
    a. M^{2+} oxidation state of group 2 acquires stable inert gas configuration.
    b. The existence of M^{2+} oxidation state in the solid state is due to $\Delta_f H^\ominus$ of MX_2 than that of MX compounds. For example,

    $\Delta_f H^\ominus$ of $MgCl = -125$ kJ mol^{-1}

    $\Delta_f H^\ominus$ of $MgCl_2 = -642$ kJ mol^{-1}

    $\therefore\ 2MgCl \longrightarrow MgCl_2 + Mg$

    $$\Delta_{\text{Disproportionation reaction}}H^\ominus = -642 - 2(-125) = -392 \text{ kJ mol}^{-1}$$

    c. The existence of M^{2+} oxidation state in aqueous solution is due to high (negative) enthalpy of hydration of M^{2+} ion which counterbalances high IE_2 value.
13. Group 2 elements are highly electropositive and hence metallic. The metallic character increases down the group (↓). But they are less metallic than group 1 elements. This is due to small size and high IE, as compared to group 1 elements. Therefore, their tendency to lose valence e^-'s is lesser than those of group 1 elements.
14. They have higher melting and boiling points as compared to those of group 2 elements because of their smaller size and more close-packed crystal lattice as compared to group 1 metals. Down the group (↓) there is no regular trend in their melting and boiling points.
15. The decreasing order of reducing character in aqueous solution decreases down the group (↓).

    The less negative value for Be is due to high (negative) hydration energy (due to the small size of Be^{2+}) and relatively high (positive) value of the enthalpy of atomisation of the metal. Hence, Be does not react with water or steam.

    $E^\ominus_{red}$ of Mg ($Mg^{2+}_{(aq)}/M_{(s)} = -2.36$ V) is more negative than that of Be, but less negative than that of Ca, Sr and Ba. Mg does not react with cold water but reacts with boiling water or steam.

    Ca, Sr and Ba react with increasing vigour even with cold water liberating H_2 and forming corresponding hydroxides.
16. **Solubility in ammonia:** Like group 1 metals, group 2 metals dissolve in liquid NH_3 to give deep blue solutions

from which the ammoniated cation $[M(NH_3)_6]^{2+}$ can be recovered. The dilute solutions are bright blue in colour due to solvated electrons but concentrated solutions are bronze coloured due to the formation of metal clusters.

17. **Formation of oxides and hydroxides:** All of them form oxides of the formula MO (M = group 2 elements). Except BeO, all the oxides have rock-salt (NaCl) (6:6) structures.

They are very stable due to quite high $\Delta_f H^\ominus$. They have high melting and boiling points, have low vapour pressure, are very good conductors of heat, are chemically inert and act as electrical insulators. That is why these oxides are used for the basic lining of furnaces and hence are used as refractory materials.

Although BeO is covalent (due to the small size of Be^{2+} ion) yet it has high melting point, because of its polymeric nature. BeO has a **wurtzite (4:4) type structure.**

All these oxides except BeO react with water to form sparingly soluble hydroxides. The reaction of these oxides with water is called *slaking*. $Be(OH)_2$ is amphoteric while others are basic.

The solubility, thermal stability and basic character of these hydroxides increase down the group (↓).

18. **Halides:** All the halides of these metals are ionic except halides of Be (e.g. BeX_2). BeX_2 exists only in gas phase but in condensed phase it exists as polymer.

The tendency to form halide hydrates gradually decreases down the group (↓). For example, $MgCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}6H_2O$, $SrCl_2{\cdot}6H_2O$ and $BaCl_2{\cdot}2H_2O$.

19. **Salts of oxoacids:**
   a. **Carbonates:** $BeCO_3$ is prone to hydrolysis and can be precipitated in the atmosphere of CO_2. The other carbonates are all sparingly soluble in water. The thermal stability of carbonates increases down the group (↓).
   b. **Sulphates:** All sulphates are white, soluble and stable to heat. The solubility of sulphates decreases down the group (↓). The high hydration (negative) enthalpies of Be^{2+} and Mg^{2+} ions overcome the lattice enthalpy factor and therefore their sulphates are soluble.
   c. **Oxalates:** The solubility of oxalates decreases down the group (↓).
   d. **Nitrates:** They are prepared by the dissolution of carbonates in dilute HNO_3. All of them decompose on heating as

   $2M(NO_3)_2 \xrightarrow{\Delta} 2MO + 4NO_2 + O_2$

   Nitrates of Sr and Ba are used in pyrotechnics for giving red and green flames.

   Thus, Ca, Sr and Ba are highly electropositive, have high negative $E^\ominus_{red}$ values and show systematic trends in the solubility of their oxo salts.

20. **Anomalous behaviour of Be:**
   a. Because of high IE, small atomic size and absence of *d*-orbitals in its valence shell, Be forms compounds which are largely covalent. Its salts are easily hydrolysed.
   b. Be shows coordination number 4 while the remaining members of this group can have a coordination number of 6 by making use of some *d*-orbitals in addition to *s*- and *p*-orbitals.
   c. It has high melting and boiling points, is harder and does not react with H_2O. Its oxides and hydroxides are amphoteric.
   d. Its carbides (e.g. Be_2C and BeC_2) are covalent while other carbides are ionic, e.g. CaC_2, Be_2C react with H_2O to give $CH_4(g)$ while Mg_2C_3 gives propyne ($H_3C-C\equiv CH$) and CaC_2, BaC_2 and SrC_2 give acetylene ($HC\equiv CH$) gas.

21. **Diagonal relationship between Be and Al:** Due to the similarity in charge density (charge/radius ratio) ($Be^{2+} = 2/31 = 0.064$ and $Al^{3+} = 3/50 = 0.060$) and same EN (Be = 1.5; Al = 1.5), they resemble in some of their properties. For example,
   a. Both are resistant to the action of acids due to a protective film of oxide on the surface.
   b. Both form soluble complexes with strong alkali, for example, beryllates $[Be(OH)_4]^{2-}$ and aluminates $[Al(OH)_4]^\ominus$.
   c. Both $BeCl_2$ and $AlCl_3$ have bridged chloride structure in vapour phase and both act as strong Lewis acids.
   d. Carbides of both, e.g. Be_2C and Al_4C_3, liberate $CH_4(g)$ on reacting with water.
   e. Both have strong tendency to form complexes, e.g. Be forms tetrahedral complexes $[BeF_4]^{2-}$ and $[Be(C_2O_4)_2]^{2-}$ whereas Al forms octahedral complexes, e.g. $[AlF_6]^{3-}$ and $[Al(C_2O_4)_3]^{3-}$.

22. **Extraction of Mg:**
   a. **From magnesite:** The ore is first calcined to form oxide which is mixed with C and heated with $Cl_2(g)$ to give $MgCl_2$. Thereafter Mg is obtained by the electrolysis of fused $MgCl_2 + NaCl + CaCl_2$ at 973–1023 K. Mg is obtained at cathode and Cl_2 is evolved at anode.
   b. **From dolomite:** The mixed oxides $[CaO{\cdot}MgO]$ obtained from the calcination of dolomite $[CaCO_3{\cdot}MgCO_3]$ are reduced with ferrosilicon (FeSi) under reduced pressure above 1273 K to give ($2Mg + Fe + Ca_2SiO_4$).
   c. **From carnallite:** The ore is dehydrated with HCl(g) and the mixture of fused KCl and $MgCl_2$ is electrolysed to give Mg as explained in the chapter (refer to Section 5.8).
   d. **From sea water:** Sea water containing $MgCl_2$ is concentrated under the sun and is treated with $Ca(OH)_2$. $Mg(OH)_2$ is precipitated, filtered and heated to give

the oxide. The oxide is reduced and electrolysed as explained in the chapter (refer to Section 5.8).

23. **Alloys of magnesium:** Some important alloys of Mg are used in automobile engines and in aeroplanes which contain 90% Mg, 2–9% Al and 1% Zn.

24. **Some important compounds of Ca and Mg:**

a. **Quicklime or calcium oxide (CaO):** It is prepared by heating limestone $CaCO_3$ at 1273 K in lime kilns. When heated in oxyhydrogen flame, it emits a brilliant white light (limelight). It absorbs moisture and CO_2 to form $Ca(OH)_2$ and $CaCO_3$, respectively.

Slaking: The addition of limited amount of H_2O disintegrates the lump of lime into a fine powder and this process is called slaking of lime. Quicklime slaked with its aqueous solution is known as **limewater** and a suspension of slaked lime in water is called **milk of lime**. It is used as a building material in the form of mortar and in the preparation of bleaching powder.

b. **Plaster of Paris ($CaSO_4 \cdot 1/2H_2O$):** It is obtained by heating gypsum ($CaSO_4 \cdot 2H_2O$) at 393 K.

$$2(CaSO_4 \cdot 2H_2O) \longrightarrow 2(CaSO_4)_2\,H_2O + 3H_2O$$

or

$$CaSO_4 \cdot 2H_2O \xrightarrow{\Delta} CaSO_4 \cdot \frac{1}{2}\,H_2O + \frac{3}{2}H_2O$$

When wetted with one-third of its weight of water, it sets with expansion into a hard mass. When heated above 473 K, it gives anhydrous $CaSO_4$ which does not set on mixing with water and is known as *dead burnt plaster*. It is used in surgical bandages, in casting, moulding and in dentistry.

c. **Magnesium sulphate ($MgSO_4 \cdot 7H_2O$) or $[Mg(H_2O)_6]SO_4 \cdot H_2O$:** It is obtained from mineral magnesite ($MgCO_3$) or dolomite [$CaMg(CO_3)_2$] on treatment with H_2SO_4. It is isomorphous with $ZnSO_4 \cdot 7H_2O$. The double salt, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ is used as a fertiliser in the name of *potash magnesis*. It is used in the fireproofing of paper and cloth and as purgative in medicine.

d. **Calcium carbonate or limestone ($CaCO_3$):** It occurs in nature as chalk, marble, corals, calcite, aragonite etc. and with Mg, as dolomite. It is used as flux in the extraction of Fe, as an antacid, in tooth paste, chewing gum, in the manufacture of high-quality paper and as a filler in cosmetics.

25. **Portland cement:** The composition of Portland cement is CaO (50–60%), SiO_2 (20–25%), Al_2O_3 (5–10%), MgO (2–3%), Fe_2O_3 (1–2%) and SO_3 (1–2%).
For good quality cement:

$$\frac{SiO_2}{Al_2O_3} = (2.5-4) \text{ and } \frac{CaO}{(SiO_2 + Al_2O_3 + Fe_2O_3)} = 2$$

The important ingredients present in cement are dicalcium silicate, $2CaO \cdot SiO_2$ (26%), tricalcium silicate, $3CaO \cdot SiO_2$ (51%) and tricalcium aluminate, $Ca_3Al_2O_6$ (11%). It is used in concrete and reinforced concrete.

26. **Biological importance of Mg and Ca:** Mg^{2+} ions are concentrated in animal cells while Ca^{2+} ions are concentrated in body fluids outside the cell. Both Mg^{2+} and Ca^{2+} catalyse a number of enzymatic reactions. The energy is stored in the form of phosphate linkage in ATP. The formation of these linkages is catalysed by Mg^{2+} and Ca^{2+} ions. However, the hydrolysis of phosphate linkage is catalysed by Ca^{2+} ions with the release of energy. The daily requirement of Ca^{2-} and Mg^{2+} ions in the human body is 200–300 mg.

27. **Some important information:**

a. Sulphates of the second group on reduction with carbon give sulphides, e.g.

$$BaSO_4 + 4C \xrightarrow{\Delta} BaS + 4CO$$

b. Magnesium perchlorate ($MgClO_4$) is used as drying agent and is called *anhydrone*.

c. $Mg(OH)_2$ is called *milk of magnesia*.

d. $Na_2SO_4 \cdot 10H_2O$ is called *Glauber's salt*.

e. **Fly ash:** It is a waste product from iron industry and has properties similar to that of cement. It mainly consists of $CaSiO_3$ (calcium silicate).

5.1 GROUP 2 ELEMENTS—ALKALINE EARTH METALS

Group 2 comprises beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra). They follow alkali metals in the periodic table. *Group 2 elements except Be are known as alkaline earth metals.* The name alkaline earth metals was initially given to magnesium, calcium, strontium and barium because they react with water to give hydroxides which are alkaline in nature.

Their oxides exist in earth's crust and are very stable to heat and fire, that is why the word 'earth' is used. All these elements have low IE, and thus behave as 'metals'.

The term has now been extended to all the elements of group 2. Radium being a radioactive element is not considered as a true representative of the alkaline earth metals.

Origin of the name:

1. The name 'beryllium' is derived from the Greek word 'beryl' which means 'to become pale'. The name was given to the metal once it was discovered that beryllium was an element in the pale semi-precious gemstone beryl.
2. The name 'magnesium' is derived from the Greek district 'Magnesia' in Thessaly. Magnesium was abundant as oxide and carbonate ore in the region and therefore became referred to as stones from Magnesia.
3. The name 'calcium' is derived from the Latin word 'calx' or 'calcis' meaning lime.
4. 'Strontium' was named after the town of 'Strontian' in Scotland, where the element strontium was first isolated from the mineral 'strontianite'.
5. The name 'barium' is derived from the Greek word 'barys' which means 'heavy'. The oxide was first called barote by Guyton de Morveau which was changed by Antoine Lavoisier to 'baryta', which was modified to 'barium'.
6. The name 'radium' originates from the Latin word 'radium' meaning 'ray' because of its ray emitting power. It was discovered by Pierre and Madam Curie in 1898 in France.

5.2 ABUNDANCE AND OCCURRENCE

Alkaline earth metals are highly reactive and hence do not occur in the free state but are widely distributed in nature in the combined state as silicates, carbonates, phosphates and sulphates.

Beryllium is the 51st most abundant element by weight found in the earth's crust. It is found in small quantities in combined state as silicates.

Beryl	$Be_3Al_2Si_6O_{18}$
Phenacite	Be_2SiO_4

Magnesium is the 6th most abundant element by weight found in the earth's crust as carbonate, sulphate and silicate.

Dolomite	$MgCO_3 \cdot CaCO_3$
Magnesite	$MgCO_3$
Epsomite	$MgSO_4 \cdot 7H_2O$
Olivine	$(Mg \cdot Fe)_2SiO_4$
Talc	$Mg_3(OH)_2Si_4O_{10}$
Chrysotile or Asbestos	$Mg_3(OH)_4Si_2O_5$
Mica	$K^{\oplus}[Mg_3(OH)_2\,(AlSi_3O_{10})]^{\ominus}$

Calcium is the 5th most abundant element in the earth's crust, and it occurs throughout the world in many common minerals. There are wide sedimentary deposits of $CaCO_3$ existing as whole mountain ranges of limestone, marble and chalk and also as coral. Other important minerals of calcium are

Fluoroapatite	$[3(Ca_3(PO_4)_2) \cdot CaF_2]$
Gypsum	$CaSO_4 \cdot 2H_2O$
Anhydrite	$CaSO_4$

Strontium and barium are much less abundant, but are well known as they occur as concentrated ores which are easy to extract. Strontium is mined as celestite ($SrSO_4$) and strontianite ($SrCO_3$). Barium is mined as barytes ($BaSO_4$).

Radium is extremely scarce and is radioactive. It was first isolated by Pierre and Marie Curie by processing many tons of the uranium ore (pitchblende).

5.3 GENERAL TRENDS IN ATOMIC AND PHYSICAL PROPERTIES

All the alkaline earth metals exhibit a striking resemblance in their physical and chemical properties with the increasing atomic number due to their similarity in electronic configuration.

The trends obtained in the variation of various atomic and physical properties are given in Table 5.1 and are explained here

Table 5.1 Atomic and physical properties of alkaline earth metals

	Elements					
Property	**Beryllium**	**Magnesium**	**Calcium**	**Strontium**	**Barium**	**Radium**
Symbol	Be	Mg	Ca	Sr	Ba	Ra
Atomic number	4	12	20	38	56	88
Atomic mass (g mol^{-1})	9.01	24.31	40.08	87.62	137.33	266.03
Electronic configuration	[He]$2s^2$	[Ne]$3s^2$	[Ar]$4s^2$	[Kr]$5s^2$	[Xe]$6s^2$	[Rn]$7s^2$
Metallic radius/(pm)	111	160	197	215	222	—

Ionic radius, M^{2+}/(pm)	31	72	100	118	135	148
Crystal structure	*hcp*	*hcp*	*fcc*	*fcc*	*bcc*	—
Melting point/(K)	1560	924	1124	1062	1002	973
Boiling point/(K)	2745	1363	1767	1655	2078	(1973)
Density/(g cm^{-3})	1.84	1.74	1.55	2.63	3.59	(5.5)
Ionisation enthalpy IE_1/ (kJ mol^{-1})	899	737	590	549	503	509
IE_2	1757	1450	1145	1064	965	979
Hydration enthalpy (kJ mol^{-1})	–2494	–1921	–1577	–1443	–1305	—
Standard potential $E^{\ominus}/(V)$ for M^{2+}/M	–1.97	–2.36	–2.84	–2.89	–2.92	–2.92
Occurrence in lithosphere (%)	2*	2.76**	4.6**	384*	390*	10^{-6}*

*ppm (parts per million).
** Percentage by weight.

5.3.1 Electronic Configuration

The electronic configuration of alkaline earth metals consists of a noble gas core with two valence electrons in the outermost ns^2 shell (Table 5.2). Therefore, the general electronic configuration of alkaline earth metals is ns^2 (where n = 2 to 7). Since all the alkaline earth metals have identical configuration, ns^2 in their valence shell, they have similar physical and chemical properties.

Table 5.2 Electronic configuration of alkaline earth metals

Element		Electronic configuration
Beryllium (Be)	(Z = 4)	[He] $2s^2$
Magnesium (Mg)	(Z = 12)	[Ne] $3s^2$
Calcium (Ca)	(Z = 20)	[Ar]$4s^2$
Strontium (Sr)	(Z = 38)	[Kr]$5s^2$
Barium (Ba)	(Z = 56)	[Xe] $6s^2$
Radium (Ra)	(Z = 88)	[Rn] $7s^2$

5.3.2 Atomic and Ionic Radii

Statement: The atomic as well as the ionic radii of the alkaline earth metals are smaller than those of the preceding alkali metal's (i.e. the corresponding member of alkali metals in the same period).

Explanation: Alkaline earth metals have greater nuclear charge as compared to alkali metals, due to which effective nuclear charge increases and the electrons are more strongly attracted towards the nuclei, causing a decrease in atomic or ionic radii.

Down the group (↓), the atomic as well as ionic radii increase with an increase in atomic number.

Statement: Radius of calcium is disproportionately larger.

Explanation: At calcium, the 3*d* and 4*s* orbitals have almost same energy. Hence, the $4s^2$ electrons are free to move to 3*d* orbital leading to an expansion in the size of the atom. Hence, the radius of calcium is disproportionately larger.

5.3.3 Ionisation Enthalpies

Statement: Alkaline earth metals have low ionisation enthalpies.

Explanation: The low ionisation enthalpies of alkaline earth metals are due to comparatively large size of their atoms, which result in weaker forces of attraction between the nucleus and valence shell electrons (ns^2).

Statement: The first ionisation enthalpies of alkaline earth metals are higher than those of corresponding group 1 metals.

Explanation: Alkaline earth metals have smaller atomic size and larger nuclear charge as compared to corresponding group 1 metal. As a result, the force of attraction between the valence shell electron and nucleus is larger in case of alkaline earth metals as compared to alkali metals. Thus, more amount of energy is required to remove the valence shell electron.

Statement: Down the group (↓), i.e. from Be to Ba, ionisation enthalpy values go on decreasing.

Explanation: Down the group (↓), atomic size increases due to the addition of new shells and increase in the magnitude of screening effect in inner shells which overweigh the effect of increased nuclear charge. As a result, the valence shell electrons are more and more loosely bound and the value of ionisation enthalpy decreases from Be to Ba.

Statement: The second ionisation enthalpies of alkaline earth metals are smaller than those of corresponding alkali metals.

Explanation: The second electron in case of alkali metals is to be removed from a cation which has already acquired a noble gas configuration. For example,

$$\underset{1s^2 2s^1}{Li_{(g)}} \xrightarrow[-e^-]{+IE_1} \underset{1s^2 2s^0}{Li^{\oplus}_{(g)}} \xrightarrow[-e^-]{+IE_2} \underset{1s^1 2s^0}{Li^{2+}}$$

(Stable noble gas configuration)

While in the case of alkaline earth metals, the second electron is to be removed from monovalent cation, which is yet to acquire the stable noble gas configuration.

$$\underset{1s^2 2s^2}{Be_{(g)}} \xrightarrow[-e^-]{+IE_1} \underset{1s^2 2s^1}{Be^{\oplus}} \xrightarrow{+IE_2} \underset{1s^2 2s^0}{Be^{2+}}$$

(Stable noble gas configuration)

Therefore, the removal of the second electron is more easy and requires less energy in case of alkaline earth metals as compared to alkali metals. Therefore, the second ionisation enthalpies of alkaline earth metals are smaller than those of corresponding alkali metals.

5.3.4 Oxidation States

Statement: Alkaline earth metals exhibit a stable oxidation state +2 in their compounds.

Explanation: The alkaline earth metals have two electrons in their valence shell and by losing these electrons, these atoms acquire stable noble gas configuration.

$$\underset{\text{(Noble gas) } ns^2}{M_{(g)}} \xrightarrow{IE_1 + IE_2} \underset{\text{(Noble gas)}}{M^{2+}_{(g)}} + 2e^{\ominus}$$

$$\underset{[Ne]3s^2}{Mg_{(g)}} \xrightarrow{IE_1 + IE_2} \underset{\substack{[Ne]3s^0 \\ \text{(Stable noble gas} \\ \text{configuration)}}}{Mg^{2+}_{(g)}} + 2e^{\ominus}$$

Statement: Even though the energy required to form M^{2+} ion, i.e. sum of first and second ionisation enthalpies, is very high, particularly for the lighter elements of the group, alkaline earth metals readily form dipositive ions, M^{2+} in their compounds.

Explanation: The first ionisation enthalpy IE_1 is nearly half of IE_2 and therefore alkaline earth metals should exhibit a stable +1 oxidation state rather than +2 oxidation state and form Mg^{2+}, Ca^{+2} ions instead of $Mg^{\oplus}$, $Ca^{\oplus}$ etc. This shows that ionisation enthalpy is not the only factor in determining the oxidation state.

Alkaline earth metals exhibit a stable +2 oxidation state in their compounds due to the following:

1. In divalent ions, M^{2+} have stable noble gas configuration, e.g.

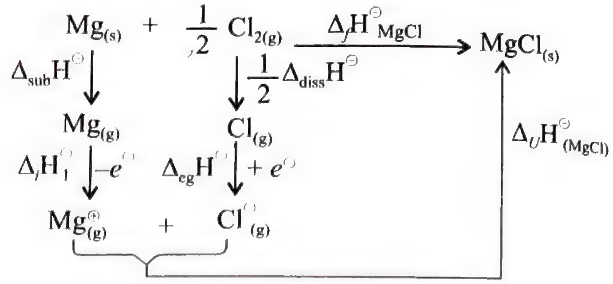
$$\underset{[Ne]3s^2}{Mg} \longrightarrow \underset{\substack{[Ne]3s^0 \\ \text{(Stable noble gas} \\ \text{configuration)}}}{Mg^{2+}} + 2e^{\ominus}$$

2. In *solid state*, the existence of divalent ions is due to greater lattice energy released when MA_2 is formed rather than MA compound; which compensates for the high second ionisation enthalpy.
3. In *aqueous state*, the existence of divalent ions is due to greater hydration enthalpy of divalent ions. The divalent ions have greater positive charge density as compared to monovalent ions. They get hydrated to greater extent and the high hydration enthalpy released compensates for the second ionisation enthalpy.

Although the second ionisation enthalpies of alkaline earth metals are almost twice of the first ionisation enthalpy, they form only bivalent rather than monovalent compounds.

This can be illustrated by making use of Born–Haber cycle for the formation of $MgCl_{(s)}$ and $MgCl_{2(s)}$.

Born–Haber cycle for the formation of $MgCl_{(s)}$:



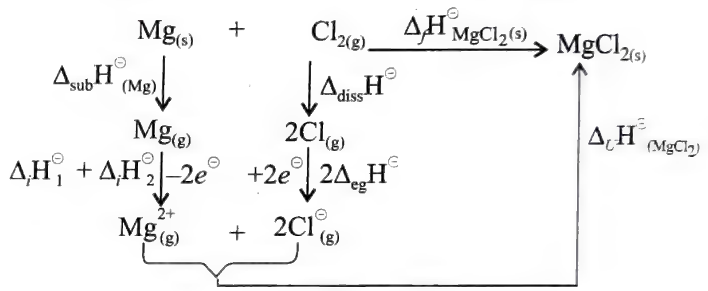
$$\Delta_f H^{\ominus}_{(MgCl)} = \Delta_{sub}H^{\ominus}_{(Mg)} + \Delta_i H^{\ominus}_{1(Mg)} + \frac{1}{2}\Delta_{diss}H^{\ominus}_{(Cl_2)} + \Delta_{eg}H^{\ominus}_{(Cl)} + \Delta_U H^{\ominus}_{(MgCl)}$$

$$= \left[150 + 737 + \frac{1}{2}(244) - 348 - 786\right] \text{kJ mol}^{-1}$$

$$= -125 \text{ kJ mol}^{-1}$$

That is, enthalpy of formation for MgCl is -125 kJ mol^{-1}.

Born–Haber cycle for the formation of $MgCl_{2(s)}$:



$$\Delta_f H^{\ominus}_{(MgCl_2)} = \Delta_{sub}H^{\ominus} + \Delta_i H^{\ominus}_{1(Mg)} + \Delta_i H^{\ominus}_{2(Mg)} + \Delta_{diss}H^{\ominus}_{(Cl_2)} + 2\Delta_{eg}H^{\ominus}_{(Cl)} + \Delta_U H^{\ominus}_{(MgCl)}$$

$$= [150 + 737 + 1450 + 244 - 2(348) - 2527] \text{ kJ mol}^{-1}$$

$$= -642 \text{ kJ mol}^{-1}$$

Thus, enthalpy of formation of $MgCl_{2(s)}$ is -642 kJ mol^{-1}. Thermodynamically, the reaction is feasible but any attempt to isolate MgCl or other $M^{\oplus}$ salts of alkaline earth metals have failed. This is due to much higher enthalpy of formation of MX_2 type of compound (e.g. $MgCl_2$) as compared to MX type of compound (e.g. MgCl).

$$Mg_{(s)} + \frac{1}{2}Cl_{2(g)} \longrightarrow MgCl_{(s)}$$

The much higher value of enthalpy of formation of MX_2 type of compound (e.g. $MgCl_2$) *leads to disproportionation of MX* (i.e. MgCl), i.e. ($2\,MgCl \rightarrow MgCl_2 + Mg$).

This can be explained with the help of the following illustration.

ILLUSTRATION 5.1

Given, the enthalpy of formation of $MgCl_{(s)}$ is -125 kJ mol^{-1} and the enthalpy of formation of $MgCl_{2(s)}$ is -642 kJ mol^{-1}. Predict whether MgCl will undergo disproportionation or not? If yes, calculate the enthalpy of disproportion.

Sol. Given,

a. $Mg_{(s)} + \frac{1}{2}Cl_{2(g)} \longrightarrow MgCl_{(s)}; \Delta H_1^{\ominus} = -125 \text{ kJ mol}^{-1}$

b. $Mg_{(s)} + Cl_{2(g)} \longrightarrow MgCl_{2(s)}; \Delta H_2^{\ominus} = -642 \text{ kJ mol}^{-1}$

c. Disproportionation of MgCl is

$$\overset{(1+)}{2MgCl_{(s)}} \longrightarrow \overset{(2+)}{MgCl_{2(s)}} + \overset{(0)}{Mg} \qquad \Delta H_3^{\ominus} = ?$$

$\therefore \Delta H_3^{\ominus} = \Delta H_2^{\ominus} - 2\Delta H_1^{\ominus}$

$= [-642 - 2(-125)] \text{ kJ mol}^{-1}$

$= -392 \text{ kJ mol}^{-1}$

Since the enthalpy of disproportionation is exothermic and much higher compared to the formation of $MgCl_{(s)}$, therefore, $MgCl_{(s)}$ will readily undergo disproportionation reaction.

Enthalpy of disproportionation of $MgCl_{(s)} = -392 \text{ kJ mol}^{-1}$.

Statement: Alkaline earth metals do not exhibit an oxidation state of +3 in their compounds or MX_3 type of compounds are not known.

Explanation: For the formation of M^{3+} ion, the third electron has to be removed from an inert gas core, which is highly stable.

$$\underset{[\text{Noble gas}]\,ns^2}{M_{(g)}} \xrightarrow[-e^{\ominus}]{IE_1} \underset{[\text{Noble gas}]\,ns^1}{M^{\oplus}} \xrightarrow{IE_2} \underset{[\text{Noble gas}]\,ns^0}{M^{2+}}$$

The third ionisation energy of these elements is too high to allow the formation of M^{3+}. Hence, MX_3 type of compounds are not known.

5.3.5 Electropositive Character or Metallic Character

Statement: Alkaline earth metals possess strong electropositive character or metallic character.

Explanation: Due to their relatively low values of ionisation enthalpies, alkaline earth metals have a strong tendency to lose both the *s*-electrons present in their valence shell (ns^2) to form dipositive ions. Thus, these elements possess strong electropositive or metallic character.

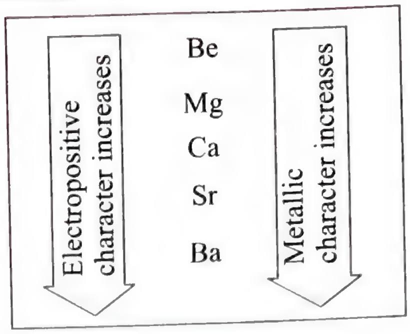
Statement: As compared to alkali metals, alkaline earth metals are less electropositive or less metallic.

Explanation: The atomic size of alkaline earth metals is small as compared to alkali metals and hence ionisation enthalpy of alkaline earth metals is more as compared to alkali metals. Consequently, alkaline earth metals have less tendency to lose valence shell electron as compared to alkali metals and hence they are less electropositive or less metallic. For example, out of Na and Mg, Mg is less electropositive or less metallic.

Statement: Down the group (↓), the electropositive or metallic character increases.

Explanation: Down the group (↓), the atomic size of alkaline earth metal increases and ionisation energy decreases. As a result, tendency to lose valence shell electron increases and electropositive or metallic character increases down the group (↓).

Electropositive character	Be < Mg < Ca < Sr < Ba
Metallic character	Be < Mg < Ca < Sr < Ba



5.3.6 Physical Properties

Statement: Alkaline earth metals as compared to alkali metals have stronger metallic bonding.

Explanation: Alkaline earth metals have stronger metallic bonding as compared to alkali metals due to:

1. Decrease in the size of the kernels.
2. Increase in the number of valence electrons available for metallic bonding.

5.3.6.1 Crystal Structure

The smaller size and stronger metallic bonding results in closer packing in the metallic lattice. In the solid state, beryllium and magnesium adopt a hexagonal closed packed structure (*hcp*), calcium and strontium a face-centred cubic structure (*fcc*) and barium a body-centred structure (*bcc*).

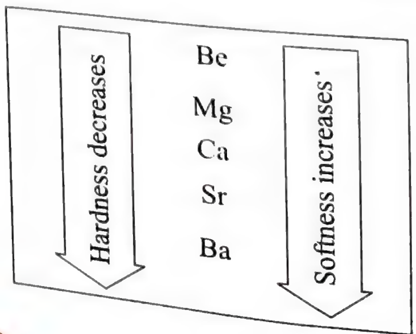
As a consequence of the closer packing in the metallic lattice, alkaline earth metals are (i) harder, (ii) denser, (iii) have high melting and boiling points and (iv) have higher heat of atomisation than alkali metals.

5.3.6.2 Hardness

Statement: The hardness decreases (or softness increases) down the group (↓) with the increase in the size of the atom.

Explanation: Beryllium bears much the same relationship with the heavier members of its group as does lithium to the other alkali metals. With their core of two rather than 8 or 18 electrons (electronic configuration of Be is $1s^2\ 2s^2$), beryllium atoms are held more tightly together. Thus beryllium in comparison to other members of its group is harder.

Down the group (↓), due to the increase in number of non-bonding electrons, repulsive forces between the atoms increases or attractive forces between the atoms decreases and hence metallic bond strength decreases. As a result, the hardness decreases (or softness increases) with the increase in the size of the atom, down the group (↓).



5.3.6.3 Density

Statement: Alkaline earth metals are denser than the alkali metals.
Explanation: As compared to alkali metals, alkaline earth metals have (i) smaller size and (ii) greater number of valence electrons available for metallic bonding.
As a result, metallic bonding is stronger and leads to better packing of crystal structure as compared to alkali metals. That is why alkaline earth metals are denser than the alkali metals.

Statement: The densities of alkaline earth metals do not show any regular trends down the group (↓). The density decreases from Be to Ca and then increases from Ca to Ba.

Explanation: This irregular trend in density can be explained on the basis of difference in crystal structure of these elements. When densities are compound for elements having the same crystal structure, the expected increase in density with increasing size does occur (due to decrease in metallic bond strength).

5.3.6.4 Melting and Boiling Points

Statement: The alkaline earth metals have higher melting and boiling points as compared to alkali metals.
Explanation: Alkaline earth metals have smaller size and greater number of valence electrons available as a result metallic bonding is stronger, which leads to more closed packed crystal lattice than alkali metals. Therefore, melting and boiling points are higher as compared to those of alkali metals.
Statement: Down the group (↓), there is no regular trends in the melting and boiling points of alkaline earth metals.
Explanation: This is due to different crystal structures adopted by the alkaline earth metals. When melting and boiling points are compared for elements having the same crystal structure, the expected decrease in melting and poiling points with increasing size does occur (due to decrease in metallic bond strength).

5.3.6.5 Thermal and Electrical Conductivity

Alkaline earth metals are good conductor of heat and electricity. On account of presence of two loosely bound valence electrons per atom which can move freely throughout the lattice structure, the alkaline earth metals are good conductor of heat and electricity.

5.3.7 Flame Colouration

Statement: Alkaline earth metals except beryllium and magnesium, impart a characteristic colour to the Bunsen flame.

Element	Be	Mg	Ca	Sr	Ba
Colour	–	–	Brick red	Crimson	Apple green

Explanation: When alkaline earth metals or their salts are exposed to the Bunsen flame, the outermost electrons of the respective atoms are excited. When these electrons come back to the ground state they emit radiations corresponding to the energy difference between the excited state and ground state in the form of visible light of particular wavelength. Giving the same amount of energy, the electrons in the atoms having higher ionisation energy will be excited to lesser excited state hence while coming back they will release lesser amount of energy which will correspond to lower frequency, i.e. higher wavelength. Calcium, therefore, emits red radiation and barium green.

In the case of beryllium and magnesium, the electrons in $2s$ and $3s$ orbitals respectively are strongly bonded to the nucleus due to their small size. Hence, they are not excited by the amount of energy available from the Bunsen flame. So, *beryllium and magnesium do not impart colour to the Bunsen flame.*

The M^{2+} ions of the alkaline earth metals are much smaller than their $M^{\oplus}$ counterparts in group 1 because of the increased nuclear charge. This leads to:

1. More hydrate formation in group 2 due to stronger ion –dipole interaction.
2. Increased covalent character of the compounds due to increased polarising power of the small, doubly charged cations.
3. Greater increase in lattice enthalpy for the corresponding compounds which results in lower solubilites.

5.3.8 Hydration Enthalpy

Statement: Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease down the group (↓).
Explanation: Down the group (↓), size of the metal ions (M^{2+}) increases, as a result the charge density (charge/radius ratio) decreases and degree of hydration decreases. Consequently, the amount of energy released on hydration, i.e. hydration enthalpy also decreases down the group (↓).

Statement: The hydration enthalpies of group 2 ions are four to five times greater than for the corresponding group 1 ions.
Explanation: This is due to the (i) size of group 2 ions which is smaller as compared to group 1 ions and (ii) charge on group 2 ions is greater as compared to group 1 ions.

As a result, the charge density (charge/radius ratio) on group 2 ion is higher as compared to group 1 ion. Consequently, group 2 ion is hydrated to greater extent and has greater hydration enthalpy as compared to group 1 ion. For example, Mg^{2+} ion has greater hydration enthalpy as compared to $Na^{\oplus}$ ion.

Due to greater degree of hydration, the crystalline compounds of group 2 have more tendency to retain the water of crystallisation than the corresponding group 1 compound. Thus, *magnesium chloride and calcium chloride exist as* $MgCl_2 \cdot 6H_2O$ *and* $CaCl_2 \cdot 6H_2O$, *whereas sodium chloride and potassium chloride exist in the anhydrous form as* NaCl *and* KCl.
Statement: Beryllium chloride exists as $BeCl_2 \cdot 4H_2O$, magnesium chloride as $MgCl_2 \cdot 6H_2O$, calcium chloride as $CaCl_2 \cdot 6H_2O$, strontium chloride as $SrCl_2 \cdot 6H_2O$, and barium chloride as $BaCl_2 \cdot 2H_2O$.
Explanation: Beryllium chloride exists as $BeCl_2 \cdot 4H_2O$ or more exactly $[Be(H_2O)_4]Cl_2$. sp^3 Hybridisation (tetrahedral)

Due to the absence of low lying d-orbitals, Be cannot expand its coordination number beyond four and hence $[(Be(H_2O)_4]^{2+}(Cl^{\ominus})_2$ is formed.

In other cases, due to the availability of low lying d-orbitals higher coordination number, i.e. 6 is achieved, e.g. $MgCl_2 \cdot 6H_2O$

actually exists as $[Mg(H_2O)_6]^{2+}$ d^2sp^3 Hybridisation (octahedral geometry)

But down the group (↓), with the increase in size of the cation (M^{2+}), charge density (charge/radius ratio) decreases and consequently degree of hydration decreases. As a result, the tendency to retain water molecule of crystallisation decreases and that is why barium chloride exists as $BaCl_2 \cdot 2H_2O$.

5.3.9 Nature of Compound Formed

Statement: Alkaline earth metals predominantly form ionic compounds. The tendency to form ionic compound increases down the group (↓). The first member Be forms covalent compounds, Mg also shows some tendency for covalence, all other elements form ionic compounds.

Explanation: Due to their low ionisation energies, alkaline earth metals predominantly form ionic compounds. The tendency to form ionic compounds increases down the group (↓), due to decrease in ionisation enthalpies from Be to Ba.

According to Fajans' rule, beryllium due to its small size and high charge density (charge/radius ratio) polarises anion to such an extent that the nature of compound becomes covalent. Down the group (↓), with the decrease in charge density of the alkaline earth metal ions, tendency to polarise the anion also decreases and the nature of the compound changes from covalent to ionic. Thus, Mg shows some tendency for covalent character, and Ca, Sr and Ba form ionic compounds.

Statement: As compared to alkali metal compounds, corresponding alkaline earth metal compounds are less ionic.

Explanation: Alkaline earth metals have smaller size and greater charge as compared to corresponding alkali metals. As a result, charge density (charge/radius ratio) of alkaline earth metal is greater and they have more tendency to polarise the anion, thus their compounds are more covalent or less ionic as compared to alkali metals.

Alternatively: Alkaline earth metals have greater ionisation energies as compared to corresponding alkali metals. As a result, they have less tendency to form cation as compared to alkali metals. Hence, alkaline earth compounds are less ionic as compared to corresponding alkali metals.

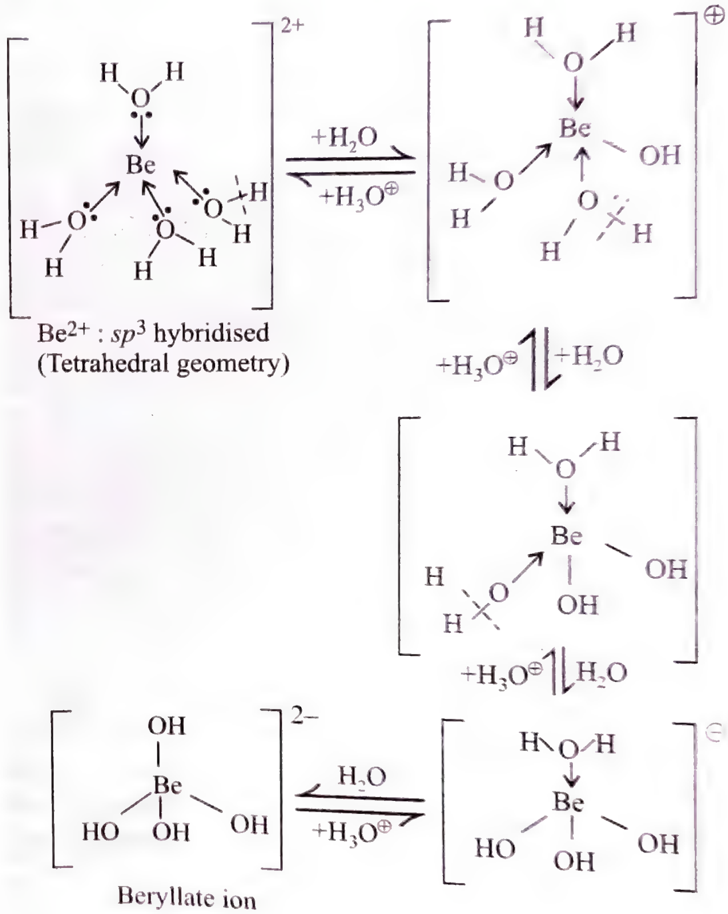
Statement: Beryllium compounds in the anhydrous state are covalent, whereas on hydration, the nature changes from covalent to ionic e.g. $BeCl_2$ is covalent whereas $BeCl_2 \cdot 4H_2O$ is ionic in nature.

Explanation: In the anhydrous state, the charge density (charge/radius ratio) of Be^{2+} is high and thus Be^{2+} has high polarising ability and it polarises the anion ($Cl^{\ominus}$) to such an extent that the compound becomes covalent. However, when hydration occurs, $[(Be(H_2O)_4]^{2+}$ is formed. The effective size of the cation increases and its polarising ability decreases and the compound, $[Be(H_2O)_4]Cl_2$, thus is ionic.

Similarly, $BeSO_4$, $Be(NO_3)_2$ are covalent, whereas $[Be(H_2O)_4]SO_4$, $[Be(H_2O)_4](NO_3)_2$ are ionic.

In water, beryllium salts have distinctively acidic character, e.g. $BeCl_2$ in water gives an acidic solution due to hydrolysis. This can be explained as follows:

In water, beryllium chloride is present in the hydrated form, i.e. $BeCl_2 \cdot 4H_2O$ or $[(Be(H_2O)_4]^{2+}(Cl)^{\ominus}_2$. Due to small size and high positive charge on Be^{2+}, the four water molecules are so strongly bound to the metal ion that oxygen–hydrogen bonds are considerably weakened, thus making the hydrolysis possible via a transfer of a proton to the solvent water molecule.



The hydrolysis is accelerated in alkaline solution, due to the removal of the protons by the hydroxyl ions. Thus in pure water, beryllium salts have distinctly acidic nature. Other group 2 metal ions, which interact less strongly with water, do not hydrolyse to appreciable extent in solution.

5.3.10 Solubility and Lattice Enthalpy

The lattice enthalpies of compounds of alkaline earth metals are much higher than that of corresponding alkali metals. This is due to the decreased size and increased charge of the ions of alkaline earth metals. For example, lattice enthalpy of $MgCl_2$ is much higher as compared to KCl.

Taking any particular anion (i) the lattice enthalpy decreases as the size of the metals increases [Lattice enthalpy $\propto 1/(r^{\oplus} + r^{\ominus})$] and (ii) the hydration enthalpy also decreases with the increase in the size of the metal ion.

For a compound to dissolve, its hydration enthalpy must exceed the lattice enthalpy.

Down the group (↓), with the increase in the size of the metal ion both lattice enthalpy and hydration enthalpy decrease.

- Decrease in lattice energy, down the group (↓) favours solubility.
- Decrease in hydration enthalpy, down the group (↓) favours insolubility.

Lattice enthalpy and hydration enthalpy thus change in opposite directions and the net result depends on which of the two has changed most.

Down the group (↓), if the lattice enthalpy decreases more rapidly than the hydration enthalpy, the solubility of the compound increases. This is true for the compounds with smaller anions like hydroxide, i.e. $Be(OH)_2$ is less soluble than $Ba(OH)_2$.

On the other hand, if the lattice enthalpy decreases less rapidly than the hydration enthalpy, the solubility of the compound decreases. This is true for compounds having larger anions like carbonates, sulphate, acetates, chromate etc.

In such cases, since the size of the cation is negligible as compared to the size of anion ($r^{\oplus} <<< r^{\ominus}$).

Lattice enthalpy thus is mainly dependent on the size of the anion and thus decreases very slowly and is not compensated by hydration enthalpy. That is why in compounds having larger anions, solubility decreases down the group (↓), e.g. $BeSO_4$ is more soluble as compared to $BaSO_4$.

5.3.11 Reducing Property

Statement: Alkaline earth metals act as strong reducing agents.

Explanation: Alkaline earth metals owing to their low ionisation enthalpy have a strong tendency to lose their valence electrons and thus behave as strong reducing agent. This is indicated by large negative values of their reduction potential.

$$M \longrightarrow M^{2+} + 2e^{\ominus}$$

Statement: Reducing character increases down the group (↓).

Explanation: Down the group (↓) from Be to Ba, ionisation energy decreases and hence tendency to lose valence electrons increases. Thus, reducing character increases from Be to Ba.

Beryllium has less negative value as compared to other alkaline earth metals. However, its reducing nature is due to large hydration enthalpy associated with the small-sized Be^{2+} ion and relatively large value of enthalpy of sublimation of beryllium.

The standard electrode potentials [$M^{2+}_{(aq)} + 2e^{\ominus} \rightarrow M_{(s)}$] of the alkaline earth metals, show that Be and Mg to certain extent are poor reductants or reducing agents than the heavier members of the group. This difference in electrode potential can be explained on the basis of the fact that electrode potential embodies all the energy changes in the process (Table 5.3).

$$M_{(s)} \xrightarrow{\Delta_{sub}H^{\ominus}} M_{(g)} \xrightarrow[-2e^{\ominus}]{IE_1+IE_2} M^{2+}_{(g)} \xrightarrow{\Delta_{hyd}H^{\ominus}} M^{2+}_{(aq)}$$

Table 5.3 Enthalpy changes for electrode half reactions

	Be	Mg	Ca	Sr	Ba
$\Delta_{sub}H^{\ominus}$ (kJ mol^{-1})	325	149	176	163	177
$IE_1 + IE_2$ (kJ mol^{-1})	2656	2187	1735	1613	1468
$\Delta_{hyd}H^{\ominus}$ (kJ mol^{-1})	−2494	−1921	−1577	−1413	−1305
$\Delta H^{\ominus}[M_{(s)} \rightarrow M^{2+}_{(aq)} + 2e^{-}]$ (kJ mol^{-1})	487	415	334	363	340

The enthalpy change is most positive for beryllium and magnesium.

Statement: Alkaline earth metals are weaker reducing agents than corresponding alkali metals.

Explanation: Since the ionisation enthalpies of alkaline earth metals are higher as compared to corresponding alkali metals, alkaline earth metals are weaker reducing agents as compared to corresponding alkali metals, e.g. Mg is weaker reducing agent as compared Na.

All the alkaline earth metals are powerful reducing agents and reduce many oxides and halides.

$$3Mg + Al_2O_3 \longrightarrow 3MgO + 2Al$$
$$2Mg + TiCl_4 \longrightarrow 2MgCl_2 + Ti$$

ILLUSTRATION 5.2

The second ionisation enthalpy of the elements of group 1 are higher than those of elements of group 2. Explain.

Sol. The second electron in case of alkali metals is to be removed from unipositive cation which has acquired highly stable noble gas configuration, e.g.

$$\underset{[Ne]3s^1}{Na} \xrightarrow[-e^-]{IE_1} \underset{[Ne]3s^0}{Na^+} \xrightarrow[-e^-]{IE_2} Na^{2+}$$

(Stable noble gas configuration)

Whereas in case of alkaline earth metals, the second electron is to be removed from a cation which will acquire the stable noble gas configuration after the removal of second electron, e.g.

$$\underset{[Ne]3s^2}{Mg} \xrightarrow[-e^-]{+IE_1} \underset{[Ne]3s^1}{Mg^{\oplus}} \xrightarrow[-e^-]{+IE_2} \underset{[Ne]3s^0}{Mg^{2+}}$$

That is why the second ionisation enthalpy of group 1 elements is much higher than those of group 2 elements.

ILLUSTRATION 5.3

What is the order of the second ionisation enthalpy of K, Ca and Ba?

Sol. K > Ca > Ba

Since the second ionisation enthalpy of alkali metals is much higher as compared to alkaline earth metals. Also, down the group (↓), ionisation energy decreases and hence the order.

ILLUSTRATION 5.4

a. Why alkaline earth metals are harder, have higher melting points and higher densities than the alkali metals?
b. Why the atoms of alkaline earth metals are smaller than the corresponding alkali metals?
c. Why alkaline earth metals have high electrical and thermal conductivities?
d. What is black ash?
e. Why the variation in physical properties of alkaline earth elements is not as regular as in the case of alkali metals?

Sol.

a. Alkaline earth metals have smaller size and stronger metallic bonding as compared to alkali metals, which results in closer packing in the metallic lattice. Consequently, alkaline earth metals are harder, have higher melting points and densities as compared to alkali metals.

b. Alkaline earth metals have greater nuclear charge as compared to alkali metals, due to which effective nuclear charge increases and the electrons are more strongly attracted towards the nucleus and the atomic size decreases.

c. Due to the presence of two loosely bound electrons in the valence shell, which can freely move throughout the crystal lattice, alkaline earth metals have high thermal and electrical conductivities.

d. Black ash is a mixture of Na_2CO_3 and CaS.

e. Since alkaline earth metals do not have the same crystal lattice structure, the variation in physical properties of alkaline earth elements is not as regular as in case of alkali metals.

ILLUSTRATION 5.5

a. Mention the most abundant and least abundant alkaline earth metal in the earth's crust.
b. Mention at least five important properties of alkaline earth metals which increase from Be to Ba.
c. Arrange alkaline earth metals in order of decreasing hydration enthalpy.
d. Ca, Sr and Ba generally form ionic compounds. Why?
e. Mention colours of Ca, Ba and Sr in flame test.

Sol.

a. Amongst the alkaline earth metals, the most abundant is **calcium** and the least abundant is **radium** in the earth's crust.

b. Five important properties of alkaline earth metals which increase from Be to Ba are:
   i. size
   ii. metallic property
   iii. reducing nature
   iv. tendency to form peroxides
   v. reactivity

c. Hydration enthalpy: $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

d. Ca, Sr and Ba generally form ionic compounds due to their low ionisation enthalpies.

e.

Elements	Ca	Sr	Ba
Flame colour	Brick red	Crimson red	Apple green

ILLUSTRATION 5.6

a. Which alkaline earth metals do not give characteristic colour to the Bunsen flame?
b. Why alkaline earth metals do not form tripositive ions?
c. Why alkaline earth metals are diamagnetic, but alkali metals are paramagnetic?
d. Why the first ionisation enthalpy of alkaline earth metals is higher than those of corresponding alkali metals?
e. Why alkaline earth metals are less electropositive than corresponding alkali metals?

Sol.

a. Be and Mg do not give characteristic colour to the Bunsen flame.

b. General electronic configuration of alkaline earth metals is ns^2 preceded by noble gas core. After the removal of two electrons, bipositive cation formed acquires a stable noble gas configuration. For the removal of the third electron, a very large amount of energy is required and that is why alkaline earth metals do not form tripositive ion, M^{3+}.

$$\underset{2p^6 3s^2}{Mg} \xrightarrow[-e^{\ominus}]{IE_1} \underset{2p^6 3s^1}{Mg^{\oplus}} \xrightarrow[-e^{\ominus}]{IE_2} \underset{\substack{2p^6 3s^0 \\ \text{Stable noble gas configuration}}}{Mg^{2+}}$$

$$Mg^{2+} \xrightarrow[-e^{\ominus}]{IE_3} \underset{2p^5 3s^0}{Mg^{3+}}$$

c. In case of alkaline earth metals, the general electronic configuration is ns^2. Due to the presence of paired electrons in their atoms, alkaline earth metals are diamagnetic. In case of alkali metals, general electronic configuration is ns^1. Due to the presence of unpaired electron, alkali metals are paramagnetic.

d. Alkaline earth metals have smaller size as compared to corresponding alkali metals due to increase in nuclear charge, as a result the higher amount of energy is required for the removal of an electron from the valence shell. That is why the first ionisation enthalpy of alkaline earth metal is higher than the corresponding alkali metal.

e. Alkaline earth metals have smaller size as compared to alkali metals. Hence, valence shell electrons are more tightly bound to the nucleus and ionisation enthalpy of alkaline earth metals is more as compared to alkali metals. Consequently, they have less tendency to lose valence shell electrons and are less electropositive as compared to alkali metals.

5.4 CHEMICAL PROPERTIES

The alkaline earth metals are less reactive than the alkali metals due to (i) decrease in size, (ii) increase in ionisation enthalpy and (iii) decrease in electropositive character.

The reactivity of alkaline earth metals increases down the group (↓) due to (i) increase in size, (ii) decrease in ionisation enthalpy and (iii) increase in electropositive character.

Chemical reactivity: Be < Mg < Ca < Sr < Ba

Some typical reactions of group 2 elements are given in Table 5.4.

Table 5.4 Some typical reactions of group 2 elements

Reaction	Remarks
With O_2: $2M + O_2 \longrightarrow 2MO$	Oxide is formed by all group 2 elements with excess oxygen.
$Ba + O_2 \longrightarrow BaO_2$	Ba also forms the peroxide.
With air: $2M + O_2 \longrightarrow 2MO$ $3M + N_2 \longrightarrow M_3N_2$	With air, all group 2 elements form a mixture of oxide (MO) and nitride (M_3N_2). Vigour of the reaction increases down the group (↓).
$M + H_2O \longrightarrow M(OH)_2 + H_2$	Be does not react with hot water or steam, Mg reacts with hot water and others react rapidly with water, forming corresponding metal hydroxide, liberating H_2.
$M + 2HCl \longrightarrow MCl_2 + H_2$	All the group 2 elements react with acids, liberating H_2.
$Be + NaOH \longrightarrow$ $Na_2[Be(OH)_4] + H_2$	Be is amphoteric.
$M + H_2 \longrightarrow MH_2$	Ionic 'salt like' hydrides are formed at high temperature by Ca, Sr, and Ba.
$3M + N_2 \longrightarrow M_3N_2$	All group 2 elements form nitrides at high temperature.
$M + X_2 \longrightarrow MX_2$	All group 2 elements form halides (X = F, Cl, Br, I)
$M + 2NH_3 \longrightarrow M(NH_2)_2 + H_2$	All the group 2 elements form amides at high temperature.

5.4.1 Reactivity Towards Air

Statement: The elements are all metallic in the appearance and possess a greyish white lustre when freshly cut, but tarnish rapidly on exposure to air.

Explanation: When the alkaline earth metals are freshly cut, the highly mobile electrons present on the surface of metal interacts with the light beam (comprising photons) striking the metal surface. As a consequence, the electrons start oscillating and like any other moving charged object, they emit electromagnetic radiations in the form of light. This light appears to be reflected from the surface of the metals, and hence the metal appears to have greyish white lustre.

On exposure to air, they tarnish rapidly due to the formation of oxide layer on the surface. With Be and Mg, the oxide layer formed on the surface is strong and continuous and there is no further reaction with moisture present in the air. But with other alkaline earth metals, the oxide layer formed on the surface reacts with the moisture. The hydroxide so formed leaves the surface which is again exposed for further attack. Therefore *Ca, Sr* and Ba are stored in paraffin but Be and Mg are not as they form a protective layer of oxide on their surface.

The reactivity towards oxygen increases down the group (↓), due to increase in electropositive nature of the elements.

Be and Mg are kinetically inert to oxygen due to the formation of thin oxide layer on their surface.

Beryllium in the massive form does not react with air below 873 K. However, powdered Be is highly reactive and burns in air to give a mixture of oxide (BeO) and nitride (Be_3N_2).

$$\underset{\text{(Air)}}{2Be + O_2} \xrightarrow{\Delta} 2BeO$$

$$\underset{\text{(Air)}}{3Be + N_2} \xrightarrow{\Delta} Be_3N_2$$

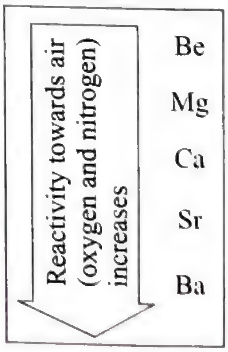
Magnesium being more electropositive than Be burns with dazzling brilliance in air to give a mixture of oxide (MgO) and nitride (Mg_3N_2).

$$\underset{\text{(Air)}}{2Mg + O_2} \xrightarrow{\Delta} 2MgO$$

$$\underset{\text{(Air)}}{3Mg + N_2} \xrightarrow{\Delta} Mg_3N_2$$

Calcium, strontium and barium being even more reactive are readily attacked by air to form a mixture of their respective oxides and nitrides.

Barium also forms peroxide on heating. Since larger cation stabilises larger anion, therefore tendency to form peroxide increases with increasing size of the metal ion (M^{2+}). Thus, BaO_2 is formed by passing air over heated Ba at 773 K.



Unlike alkali metals, the alkaline earth metals do not form superoxides when heated with oxygen.

5.4.2 Reactivity Towards Water

Statement: Beryllium does not react with water or steam even at red heat.

Magnesium does not react with cold water but react with boiling water or steam.

Ca, Sr and Ba react with cold water. Vigour of the reaction with water increases from Ca to Ba.

Explanation: Beryllium, due to the presence of protective layer of oxide on its surface survives even on heating and does not react with water.

The electrode potential of Be ($E^{\ominus}_{red}$ = −1.97 V) is least negative among the group 2 metals. This implies that Be is least electropositive and hence does not react with water or steam even at red heat.

Magnesium, due to the presence of protective oxide layer on its surface, does not react with cold water. On heating it gives

$$Mg + H_2O \xrightarrow{\Delta} MgO + H_{2(g)}$$

or

$$Mg + 2H_2O \xrightarrow{\Delta} Mg(OH)_2 + 2H_{2(g)}$$

The electrode potential of Mg ($E^{\ominus}$ = −2.37 V), although is more negative than Be, but is still less negative than those of alkali metals and hence it does not react with cold water but reacts with boiling water or steam.

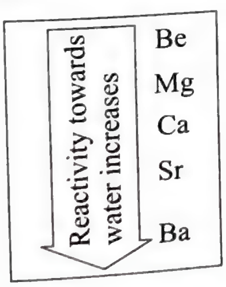
Ca, Sr and Ba react with cold water, liberating H_2 and forming the corresponding metal hydroxide.

$$M + 2H_2O \longrightarrow M(OH)_2 + H_2 \text{ (where M = Ca, Sr, Ba)}$$

Ca, Sr and Ba have more negative electrode potentials, similar to those of corresponding alkali metals and hence react vigorously even with cold water.

Reactivity of alkaline earth metals increases down the group (↓). However, the reactivity is less vigorous as compared to corresponding alkali metals.

Due to the increase in the negative value of reduction potential of alkaline earth metals the reactivity with water increases down the group (↓). Since group 2 elements have slightly less negative values of reduction potential as compared to corresponding alkali metals, alkaline earth metals are less reactive as compared to corresponding alkali metal.



5.4.3 Reactivity Towards Hydrogen

All the elements of group 2, except beryllium, combine with hydrogen on heating to form hydride of the type MH_2.

$$M + H_2 \xrightarrow{\Delta} MH_2 \quad \text{(where M = Mg, Ca, Sr, Ba)}$$

Be does not combine with H_2 at any temperature. Mg combines with H_2 only when heated with the gas under pressure, Ca, Sr and Ba combine readily with H_2 on heating, i.e. reactivity of the element towards hydrogen increases down the group (↓).

BeH_2 and MgH_2 can be conveniently prepared by reduction of $BeCl_2$ and $MgCl_2$ respectively with lithium aluminium hydride, ($LiAlH_4$) in ether.

$$2BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$$

$$2MgCl_2 + LiAlH_4 \longrightarrow 2MgH_2 + LiCl + AlCl_3$$

Some important characteristics of hydrides are as follows:

1. BeH_2 and MgH_2 are covalent and polymeric compounds. Since both have only four electrons (with two normal covalent bonds) in the valence shell, they are known as *electron deficient compounds*. To make up their electron deficiency, each Be or Mg atom forms four *three centre two electron (3c, 2e) bond* or *banana bond or tan bond* (Fig. 5.1).

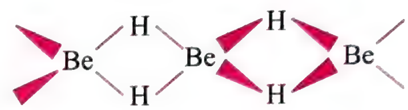


Fig. 5.1 Polymeric BeH_2 structure

   The bonding is largely covalent and it is due to the electron deficiency that BeH_2 and MgH_2 have polymeric structure. Calcium, strontium and barium hydrides are white, high melting solids. These are ionic in nature and contain hydride, $H^{\ominus}$ ion, i.e. $M^{2+}(H^{\ominus})_2$ (where M = Ca, Sr, Ba). This is evidenced by liberation of H_2 at cathode, during the electrolysis of the fused salts.

2. All the hydrides of group 2 elements react with water and liberate hydrogen, H_2, and thus behave as *reducing agents*.

   $$MH + 2H_2O \longrightarrow M(OH)_2 + 2H_2\uparrow$$

   (where M = Be, Mg, Ca, Sr, Ba)

3. CaH_2 is also known as *hydrolith* and is used for the production of hydrogen by the action of water on it.

   $$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2\uparrow$$

4. All the hydrides are thermally stable. Their thermal stability decreases from Be to Ba.

5.4.4 Reactivity Towards Halogens

Alkaline earth metals react with halogens at elevated temperature to form halides having general formula, MX_2.

$$M + X_2 \xrightarrow{\Delta} MX_2$$

(where X = F, Cl, Br, I) and (M = Be, Mg, Ca, Sr, Ba)

Alkaline earth metal halides can also be obtained by the action of halogen acids on metals, their oxides, carbonates and hydroxides.

$$M + 2HX \longrightarrow MX_2 + H_2\uparrow$$

$$MO + 2HX \longrightarrow MX_2 + H_2O$$

$$M_2CO_3 + HX \longrightarrow MX_2 + H_2O + CO_2\uparrow$$

$$M(OH)_2 + 2HX \longrightarrow MX_2 + 2H_2O$$

Thermal decomposition of $(NH_4)_2BeF_4$ is the best method for the preparation of BeF_2.

$$(NH_4)_2BeF_4 \xrightarrow{\Delta} 2NH_4F + BeF_2$$

$BeCl_2$ can be prepared by:

1. Heating BeO with Cl_2 in the presence of carbon.

   $$BeO + C + Cl_2 \xrightarrow{600-800\text{ K}} BeCl_2 + CO$$

2. Heating BeO with CCl_4

$$2BeO + CCl_4 \xrightarrow{1100\text{ K}} 2BeCl_4 + CO_2$$

5.4.5 Reactivity Towards Acids and Bases

All the elements of group 2 react with acids liberating H_2, although Be reacts slowly.

$$M + H_2SO_4 \longrightarrow MSO_4 + H_2\uparrow$$
$$M + 2HCl \longrightarrow MCl_2 + H_2\uparrow$$

(where M = Be, Mg, Ca, Sr, Ba)

Beryllium is rendered passive by concentrated HNO_3, i.e. it does not react. This is due to the fact that conc HNO_3 is a strong oxidising agent and forms a thin layer of oxide on the surface of Be, which protects it from further attack by conc HNO_3.

$$\underset{\text{(Very dilute)}}{Mg + 2HNO_3} \longrightarrow Mg(NO_3)_2 + H_2$$

$$\underset{\text{(Dilute)}}{3Mg + 8HNO_3} \longrightarrow 3Mg(NO_3)_2 + 4H_2O + 2NO$$

Beryllium being amphoteric (reacts with acids as well as bases) dissolves in cold concentrated alkalis liberating H_2 and forming corresponding alkali metal beryllate.

$$Be + 2\,NaOH + 2H_2O \longrightarrow Na_2[Be(OH)_4] + H_2$$
$$\text{or } \underset{\text{Sodium beryllate}}{NaBeO_2.\ 2H_2O} + H_2$$

5.4.6 Solution in Liquid Ammonia

Like alkali metals, all alkaline earth metals (except beryllium) dissolve in liquid ammonia giving blue solution which contain solvated electrons.

$$M + (x + 2y)\,NH_3 \longrightarrow [M(NH_3)_x]^{2+} + 2[e(NH_3)_y]^{\ominus} \quad ...(5.1)$$

All these solutions have properties similar to those of alkali metals.

Calcium, strontium and barium can be isolated from their ammonia solution as ammoniates $[M(NH_3)_6]^{2+}$. This tends to support the idea that metals dissolve in ammonia to give ammoniated species (Eq. 5.1).

Statement: Magnesium does not dissolve in liquid ammonia, but on prolonged heating, hydrogen is evolved. However, if a strong base such as KNH_2 or $NaOCH_3$ is present, a blue solution is readily formed.

Explanation: This can be explained on the basis of the fact that Mg^{2+} ion has relatively high charge density. Thus, if any magnesium does dissolve by forming ammoniate, the Mg^{2+} formed would interact with the solvent to give ammonolysis product.

$$[Mg\,(NH_3)_x]^{2+} + NH_3 \rightleftharpoons [Mg(NH_3)_{x-1}(NH_2)]^{\oplus} + NH_4^{\oplus} \ ...(5.2)$$

This reaction is analogous to the reaction in water with highly charged ions such as Al^{3+}, Be^{2+} etc. The $NH_4^{\oplus}$ ion thus formed would react with solvated electron produced during the dissolution of magnesium to give hydrogen.

$$NH_4^{\oplus} + 2[e(NH_3)_x]^{\ominus} \longrightarrow (2x + 1)\,NH_3 + \frac{1}{2}H_2\uparrow \quad ...(5.3)$$

In the presence of strong base, reaction (5.2) is suppressed resulting in negligible concentration of $NH_4^{\oplus}$ ions. Under these conditions only reaction (5.1) will occur and the solution will turn blue.

5.4.7 Complex Formation

Alkaline earth metals have more tendency to form complexes as compared to alkali metals.

Complex formation depends on:

1. Size of metal atom/ion
2. Charge on metal ion
3. Availability of empty orbitals of approximately right energy.

Alkaline earth metals have smaller size and greater charge as compared to alkali metals and that is why they are expected to have greater tendency to form complexes than the corresponding alkali metals.

The complex forming tendency decreases down the group(↓).

Down the group (↓), the charge remains the same, but size increases, as a result the charge/radius ratio decreases or positive field decreases. This results in reduced tendency to accept a pair of electron from ligands ($M^{2+} \leftarrow : L$) and hence complex forming tendency decreases down the group (↓). Thus beryllium forms many complexes and barium very few.

$$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$

Compounds of beryllium are essentially covalent and are predominantly four-coordinated complexes. Beryllium due to its high charge/radius ratio reacts with Lewis bases very readily. Beryllium fluoride readily coordinates with fluoride ions forming tetrafluoroberyllates $[BeF_4]^{2-}$ with fluorides.

$$2NaF + BeF \longrightarrow Na_2^{\oplus}\,[BeF_4]^{2-}$$

These four-coordinated complexes have tetrahedral geometry. Be^{2+} ion in $[BeF_4]^{2-}$ is sp^3 Hybridisation (tetrahedral geometry)

Due to the absence of low-lying *d*-orbitals in beryllium, it cannot expand its coordination number beyond 4. The remaining members of this group have vacant *d*-orbitals of suitable energy and hence they can expand their coordination number to 6 or more by making use of these orbitals.

Hydrated beryllium ion exists as tetrahedral $[Be(H_2O)_4]^{2+}$ ion, whereas magnesium ion exists as $[Mg(H_2O)_6]^{2+}$. $BeCl_2$ accepts lone pairs from Lewis bases forming compounds of the type $BeCl_2{\cdot}L_2$ where L is an ether, aldehyde, ketone containing lone pair on oxygen.

In contrast to the coordination behaviour of Be, the heavier members of this group form six-coordinate as well as four-coordinate compounds.

ILLUSTRATION 5.7

a. Na_2SO_4 is soluble in water whereas $BaSO_4$ is insoluble. Why?

b. When Mg metal is burnt in air, a white powder is left behind as ash. What is the white powder?

Sol.

a. The lattice enthalpy of Na_2SO_4 is less than its hydration enthalpy whereas the lattice enthalpy of $BaSO_4$ (because of +2 charge on Ba^{2+}) is very high as compared to its hydration enthalpy. That is why Na_2SO_4 is soluble in water whereas $BaSO_4$ is insoluble.

b. Magnesium on burning in air reacts with oxygen and nitrogen resulting in the formation of MgO and Mg_3N_2.

$2Mg + O_2 \longrightarrow 2MgO$

$3Mg + N_2 \longrightarrow Mg_3N_2$

White powder is the mixture of MgO and Mg_3N_2.

ILLUSTRATION 5.8

a. $[BeF_4]^{2-}$ exits, but $[BeCl_6]^{4-}$ does not. Give reason.

b. Hydrated beryllium ion exists as $[Be(H_2O)_4]^{2+}$, whereas hydrated magnesium ion exists as $[Mg(H_2O)_6]^{2+}$. Give reason.

Sol.

a. $[BeF_4]^{2-}$ exists (sp^3), but $[BeF_6]^{4-}$ does not.

Due to the absence of low-lying d-orbitals in beryllium, it cannot expand its coordination number beyond 4, hence $[BeF_4]^{2-}$ exists, but $[BeF_6]^{4-}$ does not.

b. Hydrated beryllium ion exists as $[Be(H_2O)_4]^{2+}$.

Due to the presence of only four orbitals of equivalent energy in Be^{2+} ion and due to the absence of low-lying d-orbitals in Be^{2+} ion, it can coordinate with four water molecules only, hence hydrated beryllium ion exists as $[Be(H_2O)_4]^{2+}$. sp^3 Hybridisation (Tetrahedral geometry)

Whereas in case of magnesium, due to the availability of low-lying d-orbitals of suitable energy, Mg can expand its coordination number to 6.

Hence, hydrated magnesium ion exists as $[Mg(H_2O)_6]^{2+}$. sp^3d^2 Hybridisation (octahedral geomery)

5.5 GENERAL CHARACTERISTICS OF COMPOUNDS OF THE ALKALINE EARTH METALS

The alkaline earth metals predominantly form dipositive oxidation state due to higher enthalpy of formation or higher lattice enthalpy in the solid state and higher hydration enthalpy in the aqueous solution, as already discussed. Alkaline earth metals form compounds which are predominantly ionic but less ionic than the corresponding alkali metal compounds, due to smaller size and greater charge. The general characteristics of few compounds of alkaline earth metals are discussed below.

5.5.1 Oxides

All the alkaline earth metals form monoxides, MO. Whereas Be forms only the monoxide, all the others form peroxides.

The positive field on alkaline earth metal ion, M^{2+}, is quite high due to its small size and +2 charge. These ions on combination with oxygen (O_2) attract the electron cloud on oxygen towards themselves, making the O=O bond cleave more easily and thus stabilising the monoxide, MO. This is particularly true in case of the smallest ion of the group, Be^{2+}. Hence, *beryllium forms only monoxide and not peroxide or superoxide.*

The positive field around the cations of other alkaline earth metals is not strong enough to prevent the formation of $(-O-O-)^{2-}$ in peroxide, but is strong enough to prevent the formation of $(O\cdots O)^{\ominus}$ in superoxide ion. Hence, all other group 2 elements, except Be, also form peroxides.

The monoxides of alkaline earth metals are more stable than those of alkali metals, due to more compatibility in the size of M^{2+} and O^{2-} as compared to $M^{\oplus}$ and O^{2-}, which results in higher lattice energy of alkaline earth metal monoxides.

Down the group (↓), as the size of the cation (M^{2+}) increases, the ease of formation and stability of peroxides formed also increases.

$MgO_2 < CaO_2 < SrO_2 < BaO_2$

The monoxides can be prepared by the following:

1. Heating or burning the alkaline earth metal in oxygen.

$M + O_2 \xrightarrow{\Delta} MO$ (where M = Be, Mg, Ca, Sr)

Note: BaO cannot be prepared by this method, as it forms some Ba_2O_2 also.

2. Thermal decomposition of their carbonates and sulphates.

$MCO_3 \xrightarrow{\Delta} MO + CO_2\uparrow$

(where M = Be, Mg, Ca, Sr, Ba)

$MSO_4 \xrightarrow{\Delta} MO + SO_3\uparrow$

3. BeO can also be prepared by pyrolysis of $Be(OH)_2$ or $BeSO_4$.

$Be(OH)_2 \xrightarrow{\Delta} BeO + H_2O$

$BeSO_4 \xrightarrow{\Delta} BeO + SO_3$

Some of the characteristics of oxides are as follows:

a. All the monoxides, except BeO, are ionic and have the NaCl type or rock salt structure (6:6 coordination). BeO have a covalent lattice similar to that of ZnS in wurtzite (4:4 coordination).

b. The oxides are highly stable as they have high crystal lattice energy obtained by packing doubly charged ions in a rock salt or wurtzite structure.

c. The lattice energy decreases as the radius of the cation increases. This is reflected in the melting points of the oxides (Table 5.5).

Table 5.5 Some properties of oxides

Oxide	Colour	$\Delta_f H^{\ominus}$	Structure	m.pt (°C)	Acid–base character
BeO	White	–550	Wurtzite	2550	WA
MgO	White	–690	NaCl	2800	WB
CaO	White	–623	NaCl	2600	WB
SrO	White	–590	NaCl	2450	SB
BaO	White	–545	NaCl	1950	SB

where WA = weak acid, WB = weak base, SB = strong base.

d. The following properties of the monoxides of alkaline earth metals make them useful for lining furnaces and hence are used as refractory materials.

i. High melting points
ii. Very low vapour pressure
iii. Chemical inertness
iv. Good conductors of heat
v. Electrical insulators

e. Although BeO is covalent but still it has high melting point.

Due to small size of Be^{2+} ion, BeO is covalent. BeO is polymeric and thus has high melting point. Each Be atom is tetrahedrally coordinated to four O-atoms.

f. *Reaction with water*: BeO is unreative to water, even the larger enthalpy of hydration of Be^{2+} is evidently insufficient to overcome the stabilising effect of the high lattice enthalpy.

MgO reacts slowly with water, that too only when it has not been previously heated at high temperature. CaO, SrO and BaO react with water (slake) readily.

$$MO + H_2O \longrightarrow M(OH)_2 + \text{Heat (where M = Ca, Sr, Ba)}$$

g. BeO is amphoteric, while all other alkaline earth metal oxides are basic in nature.

The amphoteric behaviour of BeO is due to small size and relatively large positive charge density on Be^{2+} ion. BeO dissolves both in the acids and alkalis, and thus it is amphoteric,

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$

$$BeO + 2NaOH \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2} + H_2O$$

Other oxides are basic in nature as they combine with water to form basic hydroxides.

$$MO + H_2O \longrightarrow M(OH)_2 + \text{Heat}$$

(where M = Mg, Ca, Sr, Ba)

Down the group (↓), with the increase in the size of the element, ionisation energy decreases and hence basic character increases.

BeO	MgO	CaO	SrO BaO
Amphoteric	Weakly basic	Basic	Strongly basic

Basic nature increases →

5.5.2 Hydroxides

Preparation: $Be(OH)_2$ and $Mg(OH)_2$ are prepared by precipitating them by addition of dilute solution of NaOH to an aqueous solution of their salts.

$$BeSO_4 + H_2O \longrightarrow Be(OH)_2\downarrow + Na_2SO_4$$

$$MgSO_4 + H_2O \longrightarrow Mg(OH)_2\downarrow + Na_2SO_4$$

$Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$ are obtained by the reaction of monoxides with water. This process is also known as *slaking*.

$$MO + H_2O \longrightarrow M(OH)_2 \text{ (where M = Ca, Sr, Ba)}$$

Some of the characteristics of the alkaline earth metal hydroxides are as follows:

1. *$Be(OH)_2$ is amphoteric whereas other hydroxides are basic. The basic strength increases down the group (↓).*

Due to small size and high ionisation enthalpy of Be, $Be(OH)_2$ is amphoteric. Therefore, it dissolves both in acids and bases.

$$Be(OH)_2 + 2HCl + 2H_2O \longrightarrow [Be(H_2O)_4]Cl_2$$

$$Be(OH)_2 + NaOH \longrightarrow Na_2BeO_2 + 2H_2O$$

Or

$$\underset{\text{sodium beryllate}}{Na_2[Be(OH)_4]}$$

Or

$$Be(OH)_2 + 2\overset{\ominus}{O}H \longrightarrow \underset{\text{Beryllate ion}}{[Be(OH)_4]^{2-}}$$

Basic strength depends upon the ease with which the hydroxide ion can be separated from the metal ion. The separation of $\overset{\ominus}{O}H$ from the base depends on the folowing:

a. Distance between M and OH in M–OH

b. Polarity of M–OH bond

Greater the polarity of the bond, greater is the ease of ionisation and hence greater is the basic strength. Down the group (↓), ionisation enthalpy decreases and hence polarity of the M–OH bond increases. Consequently, basic strength increases from $Be(OH)_2$ to $Ba(OH)_2$.

2. The hydroxides decompose on heating. The thermal stability increases down the group (↓).

$$M(OH)_2 \xrightarrow{\Delta} MgO + H_2O$$

3. Alkaline earth metal hydroxides are less basic than the corresponding alkali metal hydroxides.

This is due to (i) decrease in size of metal ions and (ii) increase in ionisation enthalpies, on moving from group 1 to group 2. As a result, M–OH bond strength increases, and ease of ionisation decreases. Thus NaOH is more basic as compared of $Mg(OH)_2$.

4. Solubility of alkaline earth metal hydroxides increases down the group (↓). *(Refer to chapter 1 also P.1.64 point 10)*

Solubility of a salt in water depends on lattice enthalpy and hydration enthalpy. Both lattice and hydration enthalpy decrease down the group (↓) with the increase in the size of cation. But lattice enthalpy decreases more rapidly as compared to hydration enthalpy and hence the solubility of MOH increases down the group (↓).

Basic strength increases ↓	$Be(OH)_2$ $Mg(OH)_2$ $Ca(OH)_2$ $Sr(OH)_2$ $Ba(OH)_2$	Solubility in water increases ↓

Aqueous solution of calcium hydroxide (limewater) and barium hydroxide (baryta) are used to detect and estimate CO_2 because they give precipitates of corresponding carbonates with CO_2.

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{White ppt}}{CaCO_3\downarrow} + H_2O$$

$$Ba(OH)_2 + CO_2 \longrightarrow \underset{\text{White ppt}}{BaCO_3\downarrow} + H_2O$$

5. Alkaline earth metal hydroxides are less soluble in water as compared to corresponding alkali metal hydroxides.

5.5.3 HALIDES

Some of the characteristics of halides are as follows:

1. Beryllium halides, BeX_2 (where X = F, Cl, Br, I) are essentially covalent due to high polarising ability of small size, highly charged Be^{2+} ion. As a result:
   a. All beryllium halides are soluble in organic solvents.
   b. They are hygroscopic and fume in moist air due to hydrolysis. On hydrolysis, they produce acidic solution.

$$BeCl_2 + \underset{\text{(Moisture)}}{2H_2O} \longrightarrow Be(OH)_2 + \underset{\text{(Fumes of HCl)}}{2HCl}$$

2. Halides of other alkaline earth metals (except Be) are ionic. Their ionic character decreases down the group (↓) due to decrease in polarising ability of M^{2+} ion with the increase in size down the group (↓).

Ionic character: $BeX_2 < MgX_2 < CaX_2 < SrX_2 < BaX_2$

With the increase in ionic character or decrease in covalent character, the tendency to hydrolyse decreases.

$BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$

3. Anhydrous beryllium halides are polymeric.

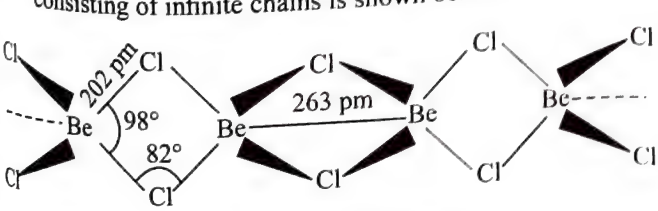
Since halides of beryllium are electron-deficient compounds as they have only four electrons in the valence shell. Therefore to complete their octet, they undergo polymerisation.

Anhydrous beryllium halides do not conduct electricity in fused state and sublime quite readily on heating. The addition of even small quantities of alkali halide to the melt considerably increases their electrical conductivity because of the formation of complex ions.

$$2\,NaF + BeF_2 \longrightarrow Na_2^{\oplus}\,[BeF_4]^{2-}$$

4. BeF_2 is glass amorphous solid of random structure, other beryllium halides are crystalline with covalent lattices.

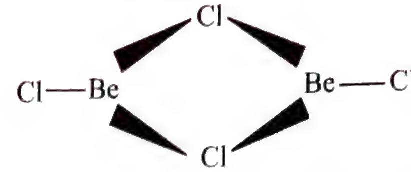
Structure of $BeCl_2$: Beryllium chloride possesses different structures in solid and vapour state. In *solid state*, it exists in the form of polymeric chain structure in which each Be atom is tetrahedrally surrounded by four chlorine atoms. Two of the chlorine atoms are bonded by covalent bonds while the other two by coordinate bond. The bridged structure consisting of infinite chains is shown below.



(Be) (sp^3 hybridised)

In the vapour state, however it exists as a monomer with a linear structure and zero dipole moment above 1200 K. But below 1200 K, it exists as dimeric structure even in vapour state.

(Monomer)
(Be; *sp* hybridised)



(Dimer) (Be; sp^2 hybridised)

5. Halides containing larger and therefore more polarisable ions like chloride, bromide, iodide show larger degree of covalency in that order.

Covalent character: $MF_2 < MCl_2 < MBr_2 < MI_2$

For example, MgF_2 possesses considerable ionic character while other magnesium halides are covalent.

According to Fajans' rule, cation remains the same, as the size of the anion increases, the tendency of the cation to polarise the electron cloud of anion also increases, which gives rise to increasing covalent character in the compound.

6. BeF_2 is highly soluble in water, whereas the other fluorides are sparingly soluble. High solubility of BeF_2 is due to high hydration enthalpy of small Be^{2+} ion which more than compensates the high lattice enthalpy of BeF_2. In case of other halides, the reduced hydration enthalpy is just not enough to compensate the lattice enthalpy, hence they are sparingly soluble. *(Refer to chapter 1 also P.1.64 point 10)*

In case of fluorides, down the group (↓) the lattice enthalpy decreases more rapidly as compared to hydration enthalpy and therefore, their solubility increases slightly along the series, hence BaF_2 is more soluble as compared to CaF_2.

The chlorides, bromides and iodides of all other elements (Mg, Ca, Sr and Ba) are ionic, have higher melting points than the fluorides and are readily soluble in water. The solubility decreases slightly down the group (↓) with the increase in size of the cation.

7. Beryllium and to certain extent magnesium halides act as Lewis acids.

8. The halides are hygroscopic and readily forms hydrates. $MgCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}6H_2O$, $SrCl_2{\cdot}6H_2O$ and $BaCl_2{\cdot}2H_2O$. However, $BeCl_2$ fumes in moist air due to hydrolysis.

9. The anhydrous salts may be obtained by dehydration of the hydrated chlorides, bromides and iodides of Ca, Sr and Ba by heating, but those of Be and Mg undergo hydrolysis.

$$CaCl_2{\cdot}6H_2O \xrightarrow{\Delta} CaCl_2 + 6H_2O$$

$$SrCl_2{\cdot}6H_2O \xrightarrow{\Delta} SrCl_2 + 6H_2O$$

$$BaCl_2{\cdot}2H_2O \xrightarrow{\Delta} BaCl_2 + 2H_2O$$

Hydrated Be and Mg halides on heating are hydrolysed by their water of crystallisation first to form the basic chloride and finally at higher temperature, oxide is produced with the evolution of HCl.

$$MgCl_2{\cdot}6H_2O \xrightarrow{\Delta} Mg(H_2O)_5(OH)Cl + HCl$$

$$Mg(H_2O)_5(OH)Cl \xrightarrow{\Delta} MgO + HCl + 5H_2O$$

$$MgCl_2{\cdot}6H_2O \xrightarrow{\Delta} MgO + 2HCl + 5H_2O$$

Anhydrous magnesium chloride may better be prepared by the action of dry Cl_2 on a mixture of MgO and carbon at dull red heat.

$$MgO + C + Cl_2 \longrightarrow MgCl_2 + CO$$

MgF_2, being more ionic is not hydrolysed so easily and may be prepared by dissolving magnesium in hydrofluoric acid, HF.

$$Mg + 2HF \longrightarrow MgF_2 + H_2$$

Bromide and iodide of magnesium are prepared by direct synthesis using anhydrous conditions.

10. Except $BeCl_2$ and $MgCl_2$, the other chlorides of group 2 impart characteristic colours to the Bunsen flame.

$CaCl_2$	Brick red
$SrCl_2$	Crimson
$BaCl_2$	Apple green

Note:

i. CaF_2 or fluorspar is the most important fluoride of group 2, as it is the only large-scale source of fluorine.

ii. Anhydrous $CaCl_2$ is used as a desiccant (i.e. drying reagent).

iii. $CaCl_2$ is widely used for melting ice on roads, particularly in cold countries, because 30% eutectic mixture of $CaCl_2$ and ice freezes at 218 K compared to NaCl and ice mixture, which freezes at 225 K.

iv. Anhydrous $MgCl_2$ is used in the electrolytic extraction of magnesium.

5.5.4 Salts of Oxoacids

Alkaline earth metals form salt of oxoacids, few of them are discussed below:

5.5.4.1 Carbonates and Bicarbonates

Preparation of carbonates: Alkaline earth metal carbonates are prepared by:

1. Passing calculated amount of CO_2 through the solution of alkaline earth metal hydroxides.

$$M(OH)_{2(aq)} + CO_{2(g)} \longrightarrow M_2CO_{3(s)} + H_2O$$

2. Adding sodium or ammonium carbonate to the aqueous solution of alkaline earth metal salt, e.g.

$$MgCl_{2(aq)} + Na_2CO_{3(aq)} \longrightarrow MgCO_{3(s)} + 2NaCl_{(aq)}$$

Properties of carbonates:

a. All the carbonates are ionic, but $BeCO_3$ is prone to hydrolysis. It contains the hydrated ion, $[Be(H_2O)_4]^{2+}$, rather than Be^{2+} and hence it is precipitated only in the atmosphere of CO_2.

$$BeCO_3 + 4H_2O \underset{\text{Presence of } CO_2}{\overset{\text{Absence of } CO_2}{\rightleftharpoons}} [Be(H_2O)_4]^{2+} + CO_3^{2-}$$

b. **Thermal stability**: All the alkaline earth metal carbonates decompose on heating to form the corresponding metal oxide and CO_2.

$$MCO_{3(s)} \xrightarrow{\Delta} MO_{(s)} + CO_{2(g)}$$

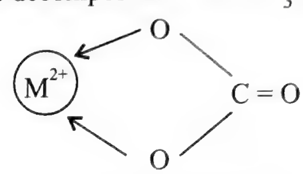
The temperature of decomposition increases from $BeCO_3$ to $BaCO_3$ (Table 5.6).

Table 5.6 Thermal stability

	$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
Decomposition temperature (°C) (Pco_2 = 1 atm)	100	540	900	1290	1360

This shows that thermal stabilities increase with the increase in atomic number of the metal.

Explanation: In the crystalline solid, the M^{2+} ion is surrounded by the oxygen of CO_3^{2-} ion. When the $\left[\frac{\text{ionic charge}}{(\text{ionic radius})^2}\right]$ ratio or polarising ability of the cation is high, a partial covalent bond is set between M and O atoms, thus weakening the C–O bond by electron withdrawal. This results in the decomposition of MCO_3 into MO and CO_2.



The large CO_3^{2-} ion can be polarised more easily by smaller cations making them more covalent and less stable, hence $BeCO_3$ is least stable and $BaCO_3$ is maximum stable.

This trend of increasing thermal stability of carbonates can also be explained on the basis of variation of lattice enthalpy of MCO_3 and MO with the increasing cation size.

$$\left[\text{Lattice enthalpy} \propto \frac{1}{r_\oplus + r_\ominus}\right]$$

The lattice enthalpy of the salt of a large anion is not particularly sensitive to the size of the cation, for the ionic separation $r_\oplus + r_\ominus$ is determined primarily by $r_\ominus$ (since $r_\oplus$ is negligible as compared to $r_\ominus$).

Therefore, the carbonate becomes only slightly less stable as the size of the cation increases. Whereas the lattice energy of an oxide MO is sensitive to the size of cation, because the radii of O^{2-} and M^{2+} are comparable.

Thus, the oxide of the smaller cation will be much more stable than those of large cations. The carbonates of smaller cations will therefore decompose to their oxides more easily than those of the larger cations.

Thermal stability:

$BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BeCO_3$

c. **Solubility in water**: The carbonates of alkaline earth metals are sparingly soluble in water and their solubility decreases down the group (↓). *(Refer to chapter 1 also P.1.64 point 10(c))*

For a compound to be soluble in water, its hydration enthalpy must exceed lattice enthalpy. Down the group (↓), both lattice enthalpy and hydration enthalpy decrease. In case of

carbonates, since radii of M^{2+} ion is negligible as compared to radii of CO_3^{2-} ion, there is very small decrease in lattice enthalpy down the group (↓).

$$\text{Lattice enthalpy} \propto \frac{1}{r_{M^{2+}} + r_{CO_3^{2-}}}$$

On the other hand, hydration enthalpy decreases rapidly. As a result, decrease in hydration enthalpy is more rapid as compared to lattice enthalpy. Thus, solubility decreases from $BeCO_3$ to $BaCO_3$.

All the alkaline earth metal carbonates are more soluble in water in the presence of CO_2, due to formation of corresponding bicarbonates.

$$MCO_{3(s)} + CO_2 + H_2O \longrightarrow M(HCO_3)_{2(aq)}$$

Bicarbonates: The bicarbonates of alkaline earth metals are prepared by passing excess of carbon dioxide, CO_2, through solution of metal hydroxide.

$$M(OH)_2 + CO_2 \longrightarrow MCO_3 + H_2O$$

$$MCO_3 + CO_2 + H_2O \longrightarrow M(HCO_3)_2$$

All the bicarbonates of alkaline earth metals are stable only in the solution and decompose on heating even in the dissolved state.

$$M(HCO_3)_2 \xrightarrow{\Delta} MCO_3 + H_2O + CO_2$$

Therefore, these cannot be isolated in the solid state and differ in this respect from the bicarbonates of alkali metals.

5.5.4.2 Nitrates

Nitrates of alkaline earth metal can be prepared in solution and are crystallised as hydrated salt by the action of nitric acid (HNO_3) on oxides, hydroxides and carbonates.

$$MO + 2HNO_3 \longrightarrow M(NO_3)_2 + H_2\uparrow$$

$$M(OH)_2 + 2HNO_3 \longrightarrow M(NO_3)_2 + 2H_2O$$

$$MCO_3 + 2HNO_3 \longrightarrow M(NO_3)_2 + CO_2 + H_2O$$

Magnesium nitrate crystallises as $Mg(NO_3)_2{\cdot}6H_2O$, whereas barium nitrate crystallises as $Ba(NO_3)_2$, an anhydrous salt. The decreasing tendency for hydration down the group (↓) is due to decreasing hydration enthalpy with increasing size of the cation, M^{2+} from Be^{2+} to Ba^{2+}.

All the nitrates on heating do not give the anhydrous salt, but decompose to give oxide.

$$2M(NO_3)_2 \xrightarrow{\Delta} 2MO + 4NO_2 + O_2$$

Anhydrous nitrates can be prepared by using liquid dinitrogen tetraoxide, N_2O_4, and ethyl acetate. Be is unusual in that it forms a basic nitrate in addition to normal salt.

$$BeCl_2 \xrightarrow{N_2O_4} Be(NO_3)_2{\cdot}2N_2O_4 \xrightarrow{50°C} Be(NO_3)_2$$

$$Be(NO_3)_2 \xrightarrow{125°C} [Be_4O(NO_3)_6]$$

Basic beryllium nitrate

Basic beryllium nitrate $(Be_4O\ (NO_3)_6)$ is covalent and has a unique structure.

5.5.4.3 Sulphates

Preparation: Alkaline earth metal sulphates are prepared by action of H_2SO_4 on metals, metal oxides, metal hydroxides and metal carbonates.

$$M + H_2SO_4 \longrightarrow MSO_4 + H_2\uparrow$$

$$MO + H_2SO_4 \longrightarrow MSO_4 + H_2O$$

$$M(OH)_2 + H_2SO_4 \longrightarrow MSO_4 + 2H_2O$$

$$MCO_3 + H_2SO_4 \longrightarrow MSO_4 + CO_2 + H_2O$$

Properties:

1. All the alkaline earth metal sulphates are white solids. Beryllium, magnesium and calcium sulphates crystallise as hydrates, i.e. $BeSO_4{\cdot}4H_2O$, $MgSO_4{\cdot}7H_2O$, $CaSO_4{\cdot}2H_2O$ but strontium and barium sulphates crystallise as anhydrous salts $SrSO_4$ and $BaSO_4$.
2. The sulphates decompose on heating to give oxides

   $$MSO_4 \xrightarrow{\Delta} MO + SO_3\uparrow$$

   The ease of decomposition decreases or thermal stability increases down the group (↓). This is evidenced by the temperature at which they decompose.

	$BeSO_4$	$MgSO_4$	$CaSO_4$	$SrSO_4$
Decomposition temperature (K)	853	1168	1422	1647

   This is due to increase in electropositive character of the metal down the group (↓) or increase in lattice enthalpy down the group (↓).
3. The solubility of the sulphates in water decreases down the group (↓). $BeSO_4$ and $MgSO_4$ are highly soluble, $CaSO_4$ is sparingly soluble but $SrSO_4$ and $BaSO_4$ are insoluble.

   For a compound to be soluble, the hydration enthalpy must be greater than lattice enthalpy. Both hydration enthalpy and lattice enthalpy decrease down the group. In case of sulphates, since the size of metal ion is negligible as compared to the size of sulphate, there is very less decrease in the lattice enthalpy down the group (↓)($U \propto 1/r^{\oplus} + r^{\ominus}$) However, hydration enthalpy decreases appreciably with the increase in size from Be^{2+} to Ba^{2+}. In other words, decrease in hydration enthalpy is more rapid as compared to lattice enthalpy. Consequently, solubility of the sulphates decreases down the group (↓).

   $$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$$

   The sulphates of alkaline earth metals are less soluble than the corresponding alkali metal sulphate.

Note:

i. The almost negligible solubility of $BaSO_4$ in water is used in the detection and estimation of SO_4^{2-} ions.

ii. $BaSO_4$ is both insoluble in water and opaque to X-rays. That is why barium meal is used to obtain a shadow of the stomach on an X-ray film which is useful in diagnosing stomach ulcers.

5.5.5 Nitrides

Statement: All the alkaline earth metals react with nitrogen on heating to give nitrides, M_3N_2.

$$3M + N_2 \xrightarrow{\Delta} M_3N_2$$

This is in contrast to the alkali metals, where only Li forms a stable nitride, Li_3N.

Explanation: Since nitrogen (N_2) is a stable molecule, large amount of energy is required to convert N_2 into N^{3-}(nitride) ion. The large amount of energy required is more than compensated by the large amount of lattice enthalpy released when the crystalline solid is formed. Nitrides of group 2 elements have high lattice energy due to small sizes and high charges of M^{2+} ion and N^{3-} ion.

Among group 1 elements only Li forms a stable nitride, Li_3N, because Li_3N has high lattice to small sizes of $Li^{\oplus}$ ion and N^{3-} ion.

The vigour of the reactions increases down the group (↓) due to increase in electropositive nature of the alkaline earth metals from Be to Ba.

Some of the characteristics of nitrides are as follows:

1. They are all colourless, crystalline ionic compounds, except Be_3N_2.
2. Be_3N_2 is covalent due to greater charge density or polarising ability of small-sized Be^{2+} ion.
3. Be_3N_2 being covalent is volatile, while other group 2 nitrides are not volatile but crystalline solids. They decompose on heating, e.g.
   $$M_3N_2 \xrightarrow{\Delta} 3M + N_2$$
4. They react with water liberating ammonia, e.g.
   $$M_3N_2 + 6H_2O \longrightarrow 3M(OH)_2 + 2NH_3$$
   (where M = Be, Mg, Ca, Sr, Ba)
5. **Reaction with CO:** The nitrides of magnesium, calcium and strontium lose nitrogen, forming the oxide when heated in carbon monoxide.
   $$M_3N_2 + 3CO \xrightarrow{\Delta} 3MO + N_2 + 3C$$
   (where M = Mg, Ca, Sr)
   Barium nitride forms cyanide on reaction with CO.
   $$Ba_3N_2 + 2CO \longrightarrow 2\,BaO + Ba(CN)_2$$

5.5.6 Carbides

Alkaline earth metals form various carbides viz. M_2C, MC_2 and M_2C_3.

M_2C type of carbide is formed only by beryllium. Be_2C is prepared as follows:

1. Direct reaction between Be and C at 1900°C.
   $$2Be + C \xrightarrow{1900°C} Be_2C$$
2. By heating BeO with carbon at 2000°C.
   $$2BeO + 2C \longrightarrow Be_2C + 2CO$$
   Be_2C is brick red coloured ionic compound and liberates methane on hydrolysis.
   $$Be_2C \longrightarrow 2Be^{2+} + C^{4-} \text{ (methanide ion)}$$
   $$Be_2C + 4H_2O \longrightarrow 2Be\,(OH)_2 + CH_4$$

MC_2 type of carbide: They are formed by all the alkaline earth metals though the preparative conditions differ; BeC_2 and MgC_2 are prepared by heating Be and Mg in acetylene, whereas CaC_2, SrC_2 and BaC_2 are prepared by heating Ca, Sr and Ba directly with carbon.

$$Be + C_2H_2 \longrightarrow BeC_2 + H_2$$
$$Ca + C \xrightarrow{1100°C} CaC_2$$

CaC_2 can also be obtained by heating CaO with C

$$CaO + C \xrightarrow{2000°C} CaC_2 + CO$$

All these carbides react with water producing acetylene:

$$CaC_2 \xrightarrow{\text{or}} Ca^{2+} + C_2^{2-} \text{ (or } \overset{\ominus}{C} \equiv \overset{\ominus}{C}\text{)}$$
(Acetylide ion)

$$CaC_2 + 2H_2O \longrightarrow Ca\,(OH)_2 + C_2H_2$$

Calcium carbide (CaC_2) is a salt containing C_2^{2-} ion and it absorbs nitrogen from air forming calcium cyanamide, $CaCN_2$ or CaNCN.

$$CaC_2 + \underset{\text{(Air)}}{N_2} \longrightarrow CaNCN + C$$

Mixture of $CaCN_2$ and carbon is known as *NITROLIM*, which is widely used as a nitrogenous fertiliser. It acts as nitrogenous fertiliser as it hydrolyses slowly over a period of months evolving ammonia (NH_3) gas.

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

M_2C_3 type of carbide: Mg_2C_3 is obtained by heating Mg with acetylene at 600°C.

$$3Mg + C_2H_2 \longrightarrow Mg_2C_3 + H_2$$

It liberates propyne on hydrolysis.

$$Mg_2C_3 \longrightarrow 2Mg^{2+} + C_3^{4-} \text{ (Propynide ion)}$$

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + \underset{\text{Propyne}}{CH_3C \equiv CH}$$

5.5.7 Sulphides

All the elements of group 2 form sulphides of the type MS corresponding to the monoxide, MO.

Preparation: BeS is formed by burning Be in sulphur vapour or by passing hydrogen sulphide (H_2S) over beryllium chloride ($BeCl_2$) at red heat.

$$BeCl_2 + H_2S \longrightarrow BeS + 2HCl$$

MgS is prepared by passing sulphur vapour over Mg at 600°C.

$$Mg + S \xrightarrow{600°C} MgS$$

Sulphides of Ca, Sr and Ba may be obtained by heating their sulphates with carbon.

$$MSO_4 + 4C \xrightarrow{\Delta} MS + 4CO \quad \text{(where M = Ca, Sr, Ba)}$$

Properties: BeS is covalent and is unaffected by water, whereas the sulphides of other alkaline earth metals are 'salt like' and hydrolyse rapidly.

$$2\,MS + 2H_2O \longrightarrow M(OH)_2 + M(SH)_2$$
$$M(SH)_2 + 2H_2O \xrightarrow{\Delta} M(OH)_2 + H_2S$$
(where M = Mg, Ca, Sr, Ba)

5.6 ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium shows anomalous behaviour, i.e. the properties of beryllium, the first member of the alkaline earth metals, differ from the rest of the members of its group. This difference is mainly because of:

1. Small size of Be atom and Be^{2+} ion.
2. High polarising power.
3. Relatively high electronegativity and ionisation energy as compared to other members.
4. Absence of *d*-orbitals in its valence shell.

Some important points of difference between beryllium and rest of the members of its group (especially magnesium) are given below:

1. Beryllium is lighter than other members of the family.
2. Beryllium has much higher melting and boiling points than the other members.
3. Beryllium does not exhibit coordination number more than four as it has only four orbitals in its valence shell.

   Be: 2*s* [⇅] 2*p* [ ][ ][ ]

   Other members of this group can have a coordination number of six by using low-lying vacant *d*-orbitals.

   Mg: 3*s* [⇅] 3*p* [ ][ ][ ] 3*d* [ ][ ][ ]

4. The oxides and hydroxides of beryllium are amphoteric, i.e. soluble in acids and bases; unlike the other member of the group.

   $BeO + 2HCl \longrightarrow BeCl_2 + H_2O$

   $BeO + 2NaOH \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2} + H_2O$

5. Beryllium does not react with water even at high temperature while other members decompose water.

   $Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2\uparrow$

6. Beryllium carbide reacts with water to give methane, while other members of the group give acetylene.

   $Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$

   $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

7. Beryllium forms fluoro-complex ion $[BeF_4]^{2-}$ in solution, whereas other members of the group do not form stable fluoro-complexes in solution.
8. Beryllium because of high charge to radius ratio forms covalent compounds, whereas other members form ionic compounds.

5.7 DIAGONAL RELATIONSHIP BETWEEN BERYLLIUM AND ALUMINIUM

Beryllium resembles aluminium, primarily due to:

1. Same electronegativity (Be = 1.5; Al = 1.5)
2. Nearly same value of charge to radius ratio

$$\left(Be^{2+} = \frac{2}{31} = 0.064;\ Al^{3+} = \frac{3}{53.5} = 0.056 \right)$$

Some of the similarities are as follows:

1. Both Be and Al are not readily attacked by acids due to the formation of invisible protective oxide film on the surface of the metal.
2. Like aluminium, beryllium forms covalent compounds.
3. The oxides and hydroxides of beryllium and aluminium are amphoteric in nature, i.e. they dissolve in acids as well as in bases.

   $BeO + 2HCl \longrightarrow BeCl_2 + H_2O$

   $BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$

   $Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$

   $Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$

   $Be(OH)_2 + 2HCl \longrightarrow BeCl_2 + 2H_2O$

   $Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$ or $Na_2[Be(OH)_4]$

   or

   $Be(OH)_2 + 2\overset{\ominus}{O}H \longrightarrow \underset{\text{Beryllate ion}}{[Be(OH)_4]^{2-}}$

   $Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$

   $Al(OH)_3 + NaOH \longrightarrow \underset{\text{Sodium metaaluminate}}{NaAlO_2} + 2H_2O$ or $Na[Al(OH)_4]$

   or

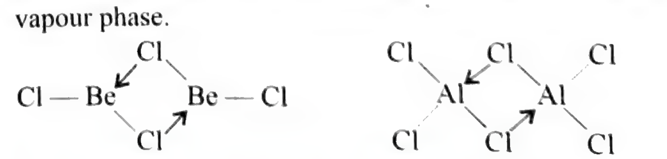
   $Al(OH)_3 + \overset{\ominus}{O}H \longrightarrow \underset{\text{Aluminate ion}}{[Al(OH)_4]^{-}}$

4. Beryllium and aluminium form fluoro-complex ions. $[BeF_4]^{2-}$ and $[AlF_6]^{3-}$ in solution.
5. The oxides of both Be and Al, i.e. BeO and Al_2O_3 are high melting insoluble solids.
6. Carbides of both Al and Be give methane gas on hydrolysis.

   $Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4\uparrow$

   $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4\uparrow$

7. Salts of Be and Al are extensively hydrolysed.
8. Both $BeCl_2$ and $AlCl_3$ act as strong lewis acids and are used in Friedel–Crafts catalysis.
9. Both $BeCl_2$ and $AlCl_3$ have bridged chloride structure in the vapour phase.



5.8 ALKALINE EARTH METALS: EXTRACTION AND USES

Magnesium: Magnesium occurs as magnesite, $MgCO_3$, dolomite, $CaMg(CO_3)_2$ or $CaCO_3{\cdot}MgCO_3$, epsomite, $MgSO_4{\cdot}7H_2O$ and carnallite, $K_2MgCl_4{\cdot}6H_2O$ or $2KCl{\cdot}MgCl_2{\cdot}6H_2O$ and langbeinite, $K_2Mg_2(SO_4)_3$ or $K_2SO_4{\cdot}2MgSO_4$ deposits. The chloride and sulphate of magnesium occur in sea water from which it is being extracted on an increasing scale.

Extractions:

1. **From magnesite or dolomite:** The ore is first calcined to form the oxide.

   $MgCO_3 \longrightarrow MgO + CO_2$

   $CaCO_3 \cdot MgCO_3 \longrightarrow CaO \cdot MgO + 2CO_2$

   The metal is obtained from the oxide or the mixed oxides as follows:

   a. From MgO—the oxide is mixed with carbon and heated in a current of chlorine gas.

   $MgO + C + Cl_2 \longrightarrow MgCl_2 + CO$

   The chloride thus obtained is subjected to electrolysis.

   b. The mixed oxides ($CaO \cdot MgO$) obtained from calcination of dolomite ($CaCO_3 \cdot MgCO_3$) are reduced by ferrosilicon under reduced pressure above 1273 K.

2. **From carnallite:** The ore is dehydrated in a current of hydrogen chloride and the mixture of fused chloride is electrolysed.

3. **From sea water (Dow's process):** Sea water containing magnesium chloride is concentrated under the sun and is treated with calcium hydroxide, $Ca(OH)_2$. Magnesium hydroxide is thus precipitated, filtered and heated to give the oxide. The oxide so obtained is treated as in (1a) above and then electrolysed.

   Anhydrous $MgCl_2$ cannot be directly obtained by heating the hydrated salt.

   If magnesium chloride hydrate, $MgCl_2 \cdot 6H_2O$ is heated strongly, it hydrolyses to yield magnesium oxide (Magnesia) which is a refractory material.

   $MgCl_2 \cdot 6H_2O \longrightarrow MgO + 2HCl + 5H_2O$

Electrolysis of magnesium chloride: Magnesium chloride obtained by any of the above methods (1 a), (2) or (3) is fused and mixed with additional mixture of sodium chloride and calcium chloride in the temperature range of 973–1023 K. The molten mixture is electrolysed. Magnesium is liberated at the cathode and chorine is evolved at the anode:

At cathode: $Mg^{2+} + 2e^{\ominus} \longrightarrow Mg$

At anode: $2Cl^{\ominus} \longrightarrow Cl_2 + 2e^{\ominus}$

A stream of coal gas is blown through the cell to prevent oxidation of magnesium metal (Fig. 5.2). Magnesium metal is obtained in liquid state, which is further distilled to give magnesium.

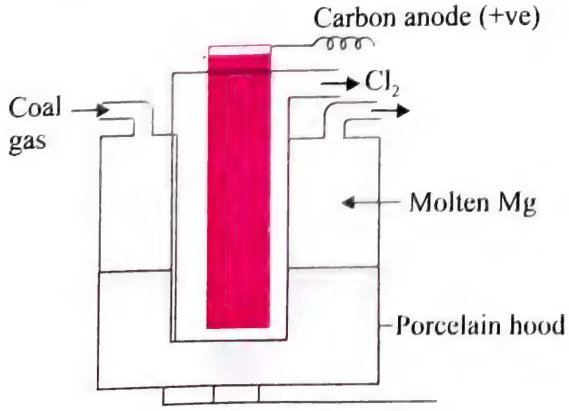


Fig. 5.2 Electrolysis of magnesium chloride

Uses: Some important uses of alkaline earth metals are as follows:

Beryllium:

1. Metallic beryllium is used for making windows of X-ray tubes due to its high transparency to X-rays.
2. Used as moderator in nuclear reactors, as beryllium absorbs fewer neutrons than any other known structural material.
3. In manufacture of alloy, copper–beryllium alloys are used in preparation of high strength springs.
4. Used to make electrodes of neon signs.

Magnesium:

1. **As an antacid:** A suspension of magnesium hydroxide in water, also known as *milk of magnesia* is used as an antacid in medicine.
2. Magnesium forms alloys with aluminium, zinc, tin and manganese. Mg–Al alloys being light in mass are used in aircraft construction.
   a. Mg = 0.5%, Mn = 0.5%, Cu = 4%, Al = 95%, used in making airships.
   b. Magnalium, Mg = 1% to 15%, Al = 85% to 99%, used in making balance beams and light instruments.
3. Used for igniting Al powder in thermite process.
4. In making Grignard reagent.
5. $MgCO_3$ is an ingredient of toothpaste.
6. Magnesium (powder and ribbon) is used in flash powders and bullbs.

Calcium:

1. Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon.
2. Owing to its reactivity with oxygen and nitrogen at elevated temperatures, it is often used to remove air from vacuum tubes.
3. For removing sulphur from petroleum.
4. As a dehydrating agent in the preparation of absolute alcohol.

Strontium:

1. Strontium chloride is used in toothpaste for sensitive teeth.
2. For producing glass (cathode ray tubes) for colour televisions.
3. Strontium salts are used in flares and fireworks for a crimson colour.

Barium: Owing to its reactivity with oxygen and nitrogen at elevated temperatures, it is often used to remove air from vacuum tubes.

Radium:

1. Radium salts are used in radiotherapy, for example in the treatment of cancer.
2. Radium salts are used in manufacture of luminous paints, which are used for painting clock and watch dials, push buttons etc. The paint consists of a mixture of sulphides of Zn, Cu, Mn etc. containing a trace of radium bromide.

ILLUSTRATION 5.9

a. Why does the solubility of alkaline earth metal hydroxides in water increase down the group.

b. Why does the solubility of alkaline earth metal carbonates and sulphates in water decrease down the group?

Sol.

a. Among alkaline earth metal hydroxides, the anion being common, the cationic radius will influence the lattice enthalpy. Since lattice enthalpy decreases much more than the hydration enthalpy with increasing ionic size, the solubility increases down the group (↓).

b. The size of anions being much larger as compared to cations, the lattice enthalpy will remain almost constant within a particular group. Since the hydration enthalpies decrease down the group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

ILLUSTRATION 5.10

$$Be_2C + H_2O \longrightarrow BeO + X$$
$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + Y$$
$$Mg_2C_3 + H_2O \longrightarrow Mg(OH)_2 + Z$$

Identify (X), (Y) and (Z).

Sol. $$Be_2C + H_2O \longrightarrow BeO + \underset{(X)}{CH_4}$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + \underset{(Y)}{C_2H_2}$$

$$Mg_2C_3 + H_2O \longrightarrow Mg(OH)_2 + \underset{(Z)}{H_2C = CHCH_3}$$

Hence, (X) $\Rightarrow CH_4$, (Y) $\Rightarrow C_2H_2$, Z $\Rightarrow H_2C = CHCH_3$

ILLUSTRATION 5.11

Give reasons for the following:

a. Alkaline earth metals cannot be obtained by chemical reduction.

b. Alkaline earth metals have stronger tendency to form complexes than alkali metals.

c. Magnesium nitride on reacting with water gives ammonia, but magnesium chloride does not give HCl on reacting with water.

Sol.

a. Alkaline earth metals cannot be obtained by chemical reduction, as they themselves are stronger reducing agents than common reducing agents. With carbon, they form carbides.

b. As compared to alkali metals, alkaline earth metal cations have

   i. Smaller size

   ii. Greater charge

   Hence, charge to radius ratio or positive field of alkaline earth metals is greater, hence they have greater tendency to form complexes.

c. Magnesium nitride, Mg_3N_2, is a salt of $Mg(OH)_2$, a strong base and NH_3, a weak acid, gets hydrolysed to give NH_3.

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

Whereas magnesium chloride, $MgCl_2$, is a salt of $Mg(OH)_2$, a strong base and HCl, a strong acid, hence it does not get hydrolysed.

ILLUSTRATION 5.12

1.0 g of magnesium ribbon was placed in a crucible and heated with the lid on, until the magnesium began to burn brilliantly. At the end of experiment, there was 1.45 g of white powder. Show that this result does not agree with the equation:

$$2Mg_{(s)} + O_{2(g)} \longrightarrow 2\,MgO_{(s)}$$

Give an explanation for your answer.

Sol. $$\underset{\substack{24 \times 2\text{ g} \\ = 48\text{ g}}}{2Mg_{(s)}} + O_{2(g)} \longrightarrow \underset{\substack{(24 + 16) \times 2\text{ g} \\ = 80\text{ g}}}{2\,MgO_{(s)}}$$

48 g of magnesium ribbon gives 80 g of MgO

$$\therefore\ 1.0\text{ g of magnesium ribbon gives} = \frac{80}{48} \times 1.0\text{ g of MgO}$$
$$= 1.66\text{ g of MgO}$$

The actual amount of white ash produced = 1.45 g

The possible reasons are:

a. Some of MgO escaped as smoke.

b. Magnesium did not react completely.

c. Magnesium might have reacted with N_2 (air) to form magnesium nitride.

5.9 SOME IMPORTANT COMPOUNDS OF MAGNESIUM AND CALCIUM

5.9.1 Magnesium Chloride ($MgCl_2 \cdot 6H_2O$)

Preparation:

1. By passing dry chlorine or HCl over heated magnesium.

$$Mg + Cl_2 \longrightarrow MgCl_2$$
$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$

2. By heating double salt; $MgCl_2 \cdot NH_4Cl \cdot 6H_2O$

$$MgCl_2 \cdot NH_4Cl \cdot 6H_2O \xrightarrow{\Delta} MgCl_2 + NH_4Cl + 6H_2O$$

Properties:

1. It is colourless, crystalline solid and higly deliquescent and soluble in water.

2. It crystallises as $MgCl_2 \cdot 6H_2O$. When heated, it decomposes as follows:

$$MgCl_2 \cdot 6H_2O \xrightarrow{\Delta} \underset{\text{Basic magnesium chloride}}{Mg(OH)Cl} + HCl + 5H_2O$$

$$Mg(OH)Cl \xrightarrow{\Delta} MgO + HCl$$

3. When a saturated solution of $MgCl_2$ is mixed with MgO, the resulting mass sets to hard marble like substance having

composition $MgCl_2 \cdot 5MgO \cdot xH_2O$. This is known as **Sorel cement or magnesia cement.**

When **Sorel** cement is mixed with dust, cork waste etc., a fairly weather proof material known as **Xylotite** is obtained.

Uses:

1. In the preparation of **Sorel** cement which is used (i) as dental filling, (ii) for cementing glass and porcelain and (iii) as a finish for plaster.
2. In the preparation of Xylotite which is used as covering for floors, laboratory tables etc.
3. For preparation of MgO and other magnesium compounds.

5.9.2 Magnesium Oxide (MgO)

Preparation: It can be prepared by the following reactions:

$$2Mg + O_2 \longrightarrow MgO$$

$$Mg(OH)_2 \xrightarrow{\Delta} MgO + H_2O$$

$$2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$$

$$\underset{\text{Magnesite}}{MgCO_3} \xrightarrow{\Delta} MgO + CO_2$$

Properties:

1. It is a light infusible white powder.
2. It is slightly soluble in water and forms magnesium hydroxide.
   $$MgO + H_2O \longrightarrow Mg(OH)_2$$
3. It is basic in nature. With water, it forms hydroxide and with acid, it forms corresponding salts.
   $$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$$
   $$MgO + H_2SO_4 \longrightarrow MgSO_4 + H_2O$$
4. It is reduced by carbon at very high temperature.
   $$MgO + C \longrightarrow Mg + CO$$

Uses:

1. In medicines, as an antacid.
2. As a refractory material for lining electric furnaces.
3. As an adsorbent in the manufacture of dynamite and in the vulcanisation of rubber.

5.9.3 Magnesium Hydroxide ($Mg(OH)_2$)

Preparation: It is prepared by dissolving magnesium in water or by treating magnesium salt with an alkali.

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2$$

$$MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2 + 2NaCl$$

Properties:

1. It is a white powder, sparingly soluble in water.
2. It is basic in nature and reacts with acids to form corresponding salts.
3. It decomposes on heating.
4. It readily dissolves in strong solution of NH_4Cl.
   $$Mg(OH)_2 + 2NH_4Cl \longrightarrow MgCl_2 + 2NH_4OH$$

Uses: In medicine, suspension of $Mg(OH)_2$ in water is used as an antacid, and is known as **milk of magnesia.**

5.9.4 Magnesium Carbonate ($MgCO_3$)

It occurs in the minerals, magnesite $MgCO_3$, dolomite $MgCO_3 \cdot CaCO_3$.

Preparation: It can be prepared by adding $NaHCO_3$ to a hot solution of magnesium salt.

$$MgSO_4 + 2NaHCO_3 \longrightarrow MgCO_3 + Na_2SO_4 + H_2O + CO_2$$

Properties:

1. It is a white powder, insoluble in water.
2. It dissolves readily in water containing excess CO_2.
   $$MgCO_3 + CO_2 + H_2O \longrightarrow Mg(HCO_3)_2$$
3. It dissolves in acids forming salts with evolution of CO_2.
   $$MgCO_3 + 2HCl \longrightarrow MgCl_2 + H_2O + CO_2\uparrow$$
   $$MgCO_3 + H_2SO_4 \longrightarrow MgSO_4 + H_2O + CO_2\uparrow$$
4. On heating, it decomposes with evolution of CO_2.
   $$MgCO_3 \xrightarrow{\Delta} MgO + CO_2\uparrow$$
5. It forms double carbonates with alkali carbonates.
   $$MgCO_3 + Na_2CO_3 \xrightarrow{\Delta} Na_2CO_3.MgCO_3$$

Uses:

1. As a filler for paper, rubber and pigments.
2. In the form of magnesite as a refractory material.
3. In the manufacture of glass and ceramics.

5.9.5 Magnesium Sulphate ($MgSO_4 \cdot 7H_2O$)

Common name: Epsom salt

Since it was formally prepared from water of Epsom spring, it occurs in nature as minerals:

1. Kieserite, $MgSO_4 \cdot H_2O$ as Stassfurt deposits
2. Epsomite, $MgSO_4 \cdot 7H_2O$ in certain gypsum deposits.

Preparation:

1. Laboratory preparation involves dissolving Mg metal or its oxide, hydroxide or carbonate in dil H_2SO_4, evaporating and crystallising out the salt.
   $$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$$
   $$MgO + H_2SO_4 \longrightarrow MgSO_4 + H_2O$$
   $$Mg(OH)_2 + H_2SO_4 \longrightarrow MgSO_4 + 2H_2O$$
   $$MgCO_3 + H_2SO_4 \longrightarrow MgSO_4 + CO_2 + H_2O$$
2. Commercially, it is prepared by extracting Kieserite with water, than the solution is filtered and the salt crystallises out.
   $$MgSO_4 \cdot H_2O + 6H_2O \longrightarrow MgSO_4 \cdot 7H_2O$$
3. By dissolving dolomite in boiling dil H_2SO_4.
   $$\underset{\text{Dolomite}}{MgCO_3 \cdot CaCO_3} + \underset{\text{dil}}{2H_2SO_4} \longrightarrow MgSO_4 + CaSO_4\downarrow + 2H_2O + 2CO_2$$

   $CaSO_4$, being insoluble in water is filtered off.

Properties:

1. It is a colourless, crystalline, efflorescent, quite soluble in water and bitter in taste.
2. It readily forms double salts with alkali metals, e.g. $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$.

3. When heated to 150°C, it changes to monohydrate. On further heating, it becomes anhydrous at 200°C. On strong heating, it decomposes into MgO.

$$MgSO_4 \cdot 7H_2O \xrightarrow{150°C} MgSO_4 \cdot H_2O \xrightarrow{200°C} MgSO_4$$

$$MgO + SO_2 + \frac{1}{2}O_2 \xleftarrow{\text{Strong heating}}$$

4. Magnesium sulphate is reduced by lampblack at 800°C.

$$2\,MgSO_4 + C \xrightarrow{800°C} 2MgO + 2SO_2 + CO_2$$

Uses:

1. As mordant in dyeing and tanning industry.
2. In the fire proofing of fabrics.
3. As a filler for paper.
4. In the soap and paint industry.
5. In dyeing cotton goods.
6. In medicine as a purgative.

5.9.6 Calcium Oxide (CaO)

Common name: Quicklime or burnt lime

Preparation: On commercial scale, it is prepared by heating limestone ($CaCO_3$) in a rotary kiln at 1070–1270 K.

$CaCO_3 \rightleftharpoons CaO + CO_2$

Since the reaction is reversible, to make the reaction proceed in forward direction, CO_2 should be removed as soon as it is formed.

Properties:

1. CaO is white amorphous solid. It has a melting point of 2870 K.
2. When heated in oxyhydrogen flame, it gives brilliant white light called limelight.
3. On exposure to atmosphere, it absorbs moisture and carbon dioxide.

   $CaO + H_2O \longrightarrow Ca(OH)_2$ (slaked lime)

   $CaO + CO_2 \longrightarrow \underset{\text{Calcium carbonate}}{CaCO_3}$

4. CaO is usually obtained in the form of lumps. On addition of limited supply of water, the lumps of lime break. This process is called *slaking of lime* and the fine powder obtained is called *slaked lime* and this process is higly exothermic.

   $CaO + H_2O \longrightarrow Ca(OH)_2 \qquad \Delta H = -62.7$ kJ

   Slaked lime or calcium hydroxide.

   The paste of lime in water is called *milk of lime*, whereas the filtered and clear solution is called *limewater*. Chemically either of these is *calcium hydroxide*.

5. Quicklime, CaO slaked with soda gives sodalime (CaO + NaOH).
6. CaO is a basic oxide and combine with acids and acidic oxides to form salts.

   $CaO + 2HCl \longrightarrow CaCl_2 + H_2O$

   $CaO + SiO_2 \longrightarrow CaSiO_3$

   $6\,CaO + P_4O_{10} \longrightarrow 2\,Ca_3\,(PO_4)_2$

7. CaO reacts with carbon dioxide (CO_2), sulphur dioxide (SO_2), hydrochloric acid (HCl) under moist conditions, but no reaction occurs when these gases are dry.

   $CaO + CO_2 \longrightarrow \underset{\text{Calcium carbonate}}{CaCO_3}$

   $CaO + SO_2 \longrightarrow \underset{\text{Calcium sulphite}}{CaSO_3}$

   $CaO + 2HCl \longrightarrow \underset{\text{Calcium chloride}}{CaCl_2} + H_2O$

Uses:

1. For the manufacture of sodium carbonate from caustic soda.
2. For the manufacture of $CaCl_2$, cement, mortar and glass.
3. For drying gases and alcohol.
4. As milk of lime in white washing and refining sugar.
5. As Limelight.
6. As limewater, it is used as laboratory reagent and in medicines.

5.9.7 Calcium Hydroxide ($Ca(OH)_2$)

Common name: Slaked lime

Preparation:

1. On commercial scale, it is prepared by addition of water to quicklime

   $CaO + H_2O \longrightarrow Ca(OH)_2$

   This process is known as slaking of lime and $Ca(OH)_2$, therefore is known as slaked lime.

2. By the reaction of calcium chloride with caustic soda.

   $CaCl_2 + 2NaOH \longrightarrow Ca(OH)_2 + 2NaCl$

Properties:

1. It is white amorphous powder, which is sparingly soluble in water. The suspension or paste of $Ca(OH)_2$ in water is called *milk of lime*, whereas the filtered and clear solution in water is called *limewater*.
2. Reaction with carbon dioxide—When carbon dioxide gas is passed through limewater, it turns milky due to the formation of calcium carbonate.

   $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O$

   On passing excess of CO_2 gas, the milkiness disappears as the precipitate, $CaCO_3$, reacts with CO_2 to form calcium bicarbonate or calcium hydrogen carbonate which is soluble in water.

   $CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$

3. Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder.

   $2\,Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2 + Ca(OCl)_2 + 2H_2O$

Uses:

1. For the preparation of bleaching powder, mortar (i.e. a building material).
2. In white wash due to its disinfectant nature.
3. In glass making and tanning industry.
4. In purification of sugar.

5.9.8 Calcium Carbonate ($CaCO_3$)

Calcium carbonate is found in nature as (i) limestone, (ii) chalk, (iii) marble and (iv) in mineral dolomite, $CaCO_3 \cdot MgCO_3$

Preparation:

1. By passing CO_2 through $Ca(OH)_2$.

   $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$

2. By addition of aqueous solution of sodium carbonate to calcium chloride.

   $Na_2CO_3 + CaCl_2 \longrightarrow 2NaCl + CaCO_3\downarrow$

Properties:

1. $CaCO_3$ is a white fluffy powder, almost insoluble in water.
2. It is insoluble in water, but dissolves when excess of CO_2 is passed through the solution, due to the formation of calcium bicarbonate or calcium hydrogen carbonate.

   $CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$

3. $CaCO_3$ decomposes to evolve CO_2, when heated to 1200 K.

   $CaCO_3 \xrightarrow{1200K} CaO + CO_2\uparrow$

4. $CaCO_3$ reacts with dilute acids to liberate CO_2.

   $CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$

   $CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$

Uses:

1. As an antacid, as mild abrasive in toothpastes, and as a filler in cosmetics, a constituent of chewing gum.
2. Calcium carbonate along with magnesium carbonate is used as flux in the extraction of metals such as iron.
3. Specially precipitated $CaCO_3$ is extensively used in the manufacture of high quality paper.
4. As a building material in the form of marble.
5. In the manufacture of quicklime, cement, washing soda and glass.

5.9.9 Calcium Chloride ($CaCl_2 \cdot 6H_2O$)

In occurs in sea water.

Preparation: In laboratory, it can be prepared by the action of hydrochloric acid on calcium, its oxide (lime) or carbonate.

$Ca + 2HCl \longrightarrow CaCl_2 + H_2\uparrow$

$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$

$CaCO_3 + HCl \longrightarrow CaCl_2 + CO_2\uparrow + H_2O$

On evaporating the resulting solution to a syrup and then cooling, colourless hexagonal crystals of $CaCl_2 \cdot 6H_2O$ are obtained.

Properties:

1. On heating at 473 K, $CaCl_2 \cdot 6H_2O$ loses four water molecules to form dihydrate $CaCl_2 \cdot 2H_2O$ and finally becomes anhydrous on fusion.

   $CaCl_2 \cdot 6H_2O \xrightarrow{473\text{ K}} CaCl_2 \cdot 2H_2O \longrightarrow CaCl_2$

   The anhydrous salt is an excellent drying agent.
2. Calcium chloride is a deliquescent substance and extremely hygroscopic.
3. It is extremely insoluble in water, but soluble in alcohol and ammonia due to the formation of $CaCl_2 \cdot 4CH_3OH$, $CaCl_2 \cdot 8NH_3$. Hence, it cannot be used as drying agent for these substances.

Uses:

1. The anhydrous salt is used as a drying agent.
2. The hydrated compound is used for making freezing mixtures and in refrigeration.
3. Highly concentrated solution of calcium chloride is used in liquid baths for heating purposes.
4. It is also sprinkled on roads to keep them wet and to prevent dust from flying.

5.9.10 Calcium Sulphate

Chemical formula	Common name or commercial name	Chemical name
$CaSO_4 \cdot 2H_2O$	Gypsum	Calcium sulphate dihydrate
$CaSO_4 \cdot \frac{1}{2}H_2O$	Plaster of Paris	Calcium sulphate hemihydrate
$CaSO_4$	Anhydrite or Dead burnt plaster	Anhydrous calcium sulphate

Preparation:

1. Gypsum can be prepared by adding dil H_2SO_4 to the solution of calcium salt.

   $CaCl_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HCl$

2. Plaster of Paris is obtained when gypsum is heated to 393 K.

   $CaSO_4 \cdot 2H_2O \xrightarrow{393\text{ K}} CaSO_4 \cdot \frac{1}{2}H_2O + \frac{3}{2}H_2O$

   or

   $2(CaSO_4 \cdot 2H_2O) \xrightarrow{393\text{ K}} 2(CaSO_4) \cdot H_2O + 3H_2O$

3. Anhydrous calcium sulphate is formed when plaster of Paris is heated to 393 K.

   $CaSO_4 \cdot \frac{1}{2}H_2O \xrightarrow{393\text{ K}} CaSO_4 + \frac{1}{2}H_2O$

   Anhydrous calcium sulphate is also known as *dead burnt plaster* or anhydrite.

Properties of gypsum:

1. It is crystalline and sparingly soluble in water.
2. It forms double salt with ammonium sulphate;

   $CaSO_4 \cdot (NH_4)_2SO_4 \cdot H_2O$.
3. Action of heat: When heated to ~393 K, gypsum forms plaster of Paris.

Properties of plaster of Paris:

1. Calcium sulphate hemihydrate is a white powder.
2. It exhibits a remarkable property of setting with water. When mixed with water (one third of its weight), it forms a plastic mass and quickly sets to a hard porous mass within 5–15 minutes. This process is highly exothermic. During the setting, a slight expansion (~1%) in volume occurs so that

it fills the mould completely and takes a sharp impression. The process of setting takes place in two steps.

a. Setting step
b. Hardening step

$$CaSO_4\cdot\frac{1}{2}H_2O \xrightarrow[\text{Setting step}]{+\frac{3}{2}H_2O} \underset{\text{(Orthorhombic form)}}{CaSO_4\cdot 2H_2O} \xrightarrow[\text{step}]{\text{Hardening}} \underset{\text{(Monoclinic form)}}{CaSO_4\cdot 2H_2O}$$

Final product of the setting process is gypsum. The setting of plaster of Paris may be catalysed by NaCl, while it is retarded by alum or borax.

3. Reaction with carbon: On strongly heating with carbon, plaster of Paris forms calcium sulphide.

$$CaSO_4 + 4C \longrightarrow \underset{\text{Calcium sulphide}}{CaS} + 4CO$$

4. A suspension of gypsum when saturated with ammonia and CO_2 forms ammonium sulphate ($(NH_4)_2SO_4$), a nitrogeneous fertiliser.

$$CaSO_4 + 2NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2SO_4 + CaCO_3$$

Properties of dead burnt plaster:

1. Anhydrous $CaSO_4$ unlike plaster of Paris does not set with water and absorbs water only slowly (like naturally occurring anhydrite).
2. On strong heating, a slight decomposition takes place.

$$CaSO_4 \xrightarrow[\text{heating}]{\text{Strong}} CaO + SO_2 + O_2$$

Uses of gypsum:

1. It is used in surgery for plastering (i.e. setting) the fractured bones.
2. In making castes for statues, in dentistry, surgical instruments etc.
3. In making black board chalks.

5.9.11 Cement

Cement is an important building material, which was first introduced in 1824 by Joseph Aspdin, a mason of Leeds, England. He found that when a strongly heated mixture of limestone and clay were mixed with water and allowed to stand, it hardened to stone-like mass which resembled Portland rock, a famous building stone of England those days. He, therefore, named it as Portland cement.

Cement is a dirty greenish heavy powder which is a mixture of limestone, silica along with oxides of aluminium, iron and magnesium.

Average composition of Portland cement:

Lime	CaO	50–60%
Silica	SiO_2	20–25%
Alumina	Al_2O_3	5–10%
Magnesium oxide	MgO	2–3%
Iron (III) oxide	Fe_2O_3	1–2%
Sulphur trioxide	SO_3	1–2%

For a good quality cement, the ratio of silica (SiO_2) to alumina (Al_2O_3) should be between 2.5 and 4.0, and the ratio of lime (CaO) to the total of oxides of silicon (SiO_2), aluminium (Al_2O_3) and iron (Fe_2O_3) should be as close as possible to 2.

$$\frac{\%SiO_2}{\%Al_2O_3} = 2.5 \text{ to } 4$$

$$\frac{\%CaO}{\%SiO_2 + \%Al_2O_3 + \%Fe_2O_3} = 2$$

1. Cement containing no iron is white, but hard to burn.
2. If the lime present is less than given by the above ratio, cement is low in strength and sets very soon.
3. If the lime present is more than given by the above ratio, the cement cracks.
4. Excess of silica produces a low hardening cement.
5. Excess of alumina produces a quick setting product.

Raw materials used for the manufacture of cement:

1. Limestone ($CaCO_3$)—It produces lime (CaO).
2. Clay—It is $Al_2O_3\cdot SiO_2\cdot Fe_2O_3\cdot 2H_2O$. Clay provides silica ($SiO_2$), alumina ($Al_2O_3$). Some of the clays do not contain Fe_2O_3 and the cement obtained in this case is white and hard to burn.
3. Gypsum ($CaSO_4\cdot 2H_2O$)—The addition of gypsum decreases the setting time of cement.

Xylotite, a weather proof material is obtained by mixing sorel cement with dust, cork waste etc.

5.9.11.1 Manufacture of Cement

Following steps are involved in the manufacture of cement:

1. **Preparation of raw meal or slurry:** The raw material, namely limestone and clay are mixed in proper proportion by either of the processes discussed below:
   a. **Dry process:** This process is employed when the raw materials, namely limestone and clay are hard.
      Limestone is first broken into small pieces. Then, clay is mixed to it in proper proportions and the mixture is pulverised to fine powder so that it can pass through a 100 mesh sieve. The homogeneous mass so produced is known as *raw meal.*
   b. **Wet process:** This process is employed when the raw materials, namely limestone and clay are soft, climate is fairly damp and fuel is cheap.
      Limestone is crushed to suitable size and clay is washed with water in wash mills to remove foreign materials, like flint. The powdered limestone is mixed with clay paste in the ratio 3:1, and the mixture is finely ground and made homogeneous. The resulting paste is known as slurry and contains about 40% water.
2. **Calcination of raw meal or slurry:** Raw meal or slurry prepared by the above-mentioned methods is introduced into the rotary kiln with the help of screw conveyer. The

rotary kiln consists of a long steel cylinder 6–8 feet in diameter and 100–250 feet in length, which is lined inside with fire bricks (Fig. 5.3). The kiln rotates on its axis at the rate of 1/2 to 1 revolution per minute. When the kiln rotates, the charge slowly moves downwards because of the rotary motion of the kiln. When it reaches the lowest part of the kiln, the temperature is about 1500°C, which is the maximum temperature of the kiln. This zone of the kiln is called maximum temperature zone. The charge takes 2–3 h to cover the journey in the kiln.

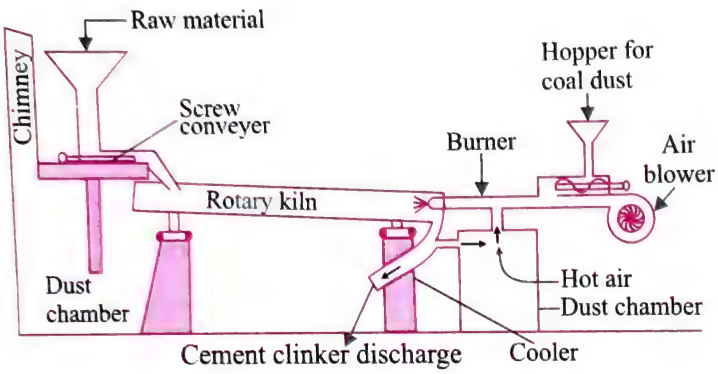


Fig. 5.3 Manufacture of Portland cement

Various reactions taking place in the rotary kiln are as follows:

a. In the moderate temperature zone or upper part of the kiln:

i. In this zone, temperature is up to 800°C.

ii. Free moisture is removed and clay is broken into oxides of aluminium, silica and iron.

$$\underset{\text{(Clay)}}{Al_2O_3\cdot SiO_2\cdot Fe_2O_3\cdot 2H_2O} \longrightarrow Al_2O_3 + SiO_2 + Fe_2O_3 + H_2O$$

b. In average temperature zone or middle of the kiln:

i. In this zone, temperature is 800–1000°C.

ii. Limestone decomposes to lime and carbon dioxide.

$$\underset{\text{Lime stone}}{CaCO_3} \longrightarrow \underset{\text{Lime}}{CaO} + \underset{\text{Carbon dioxide}}{CO_2}$$

c. In maximum temperature zone or lower part of the kiln:

i. In this zone, temperature is 1000–1500°C.

ii. The oxides, viz. CaO, SiO_2, Al_2O_3 and Fe_2O_3 combine to form calcium silicates, aluminates and ferrite.

$$2\,CaO + SiO_2 \longrightarrow \underset{\text{Dicalcium silicate}}{2CaO\cdot SiO_2}$$

$$3\,CaO + SiO_2 \longrightarrow \underset{\text{Tricalcium silicate}}{3CaO\cdot SiO_2}$$

$$2\,CaO + Al_2O_3 \longrightarrow \underset{\text{Dicalcium aluminate}}{2CaO\cdot Al_2O_3}$$

$$3\,CaO + Al_2O_3 \longrightarrow \underset{\text{Tricalcium aluminate}}{3CaO\cdot Al_2O_3}$$

$$4\,CaO + Al_2O_3 + Fe_2O_3 \longrightarrow \underset{\text{Tetracalcium aluminoferrite}}{4CaO\cdot Al_2O_3\cdot Fe_2O_3}$$

The resulting product is known as Cement Clinker, which is greenish black or grey coloured balls ranging in size from small nuts to peas.

3. Addition of gypsum to cement clinker: The cooled cement clinker is mixed with 2–3% of its weight of gypsum ($CaSO_4\cdot 2H_2O$).

Flow diagram of the manufacture of cement is as given below.

Limestone and clay are powdered and mixed to prepare **Raw Meal or Slurry**

→ Calcination in Rotary kiln →

Cement Clinker
Main constituent:
$2CaO\cdot SiO_2$, $3CaO\cdot SiO_2$, $2CaO\cdot Al_2O_3$, $4CaO\cdot Al_2O_3\cdot Fe_2O_3$

↓ Addition of gypsum

Portland cement

5.9.11.2 Setting of Cement

When the cement is mixed with water, it absorbs water to form initially a gelatinous mass which slowly sets into a hard mass and very resistant to pressure. This is known as setting of cement.

Reactions involved in the setting of cement are as follows:

1. During the first 24 hours:

a. When cement is mixed with water, tricalcium aluminate, $3CaO\cdot Al_2O_3$, absorbs water and forms a colloidal gel of composition $3CaO\cdot Al_2O_3\cdot 6H_2O$.

$$3CaO\cdot Al_2O_3 + 6H_2O \longrightarrow \underset{\text{Hydrated colloidal gel of tricalcium aluminate}}{3CaO\cdot Al_2O_3\cdot 6H_2O}$$

This gel slowly crystallises.

b. Tricalcium aluminate, $3CaO\cdot Al_2O_3$, which is a fast setting material, reacts with gypsum to form calcium sulphoaluminate.

$$3CaO\cdot Al_2O_3 + \underset{\text{(Gypsum)}}{2(CaSO_4\cdot 2H_2O)} + 2H_2O \longrightarrow \underset{\text{Calcium sulphoaluminate}}{3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 2H_2O} + 6H_2O$$

Thus, addition of gypsum removes the fast setting constituent of the clinker and hence the setting process of cement gets retarded and results in the better strength of the mass that sets.

2. Between 1 and 7 days:

$3CaO\cdot SiO_2$ and $3CaO\cdot Al_2O_3$ get hydrolysed.

$$3CaO\cdot SiO_2 + H_2O \xrightarrow{\text{Hydrolysis}} Ca(OH)_2 \text{ ppt.} + \underset{\text{(Amorphous)}}{2CaO\cdot SiO_2}$$

$$3CaO\cdot Al_2O_3 + 6H_2O \xrightarrow{\text{Hydrolysis}} 3\,Ca(OH)_2\downarrow + 2Al(OH)_3\downarrow$$

$Ca(OH)_2$ formed above changes into needle shape crystals which gets studded in the colloidal gel, $2CaO\cdot SiO_2$, thus

increasing its strength. $Al(OH)_3$ formed above fills the interstices resulting in hardening of the mass.

3. **Between 7 and 28 days:**
   a. $2\,CaO{\cdot}SiO_2$ begins to hydrate a slow reaction and forms the hydrated colloidal gel ($2CaO{\cdot}SiO_2{\cdot}xH_2O$)

$$2\,CaO{\cdot}SiO_2 + xH_2O \xrightarrow{\text{Hydration}} \underset{\text{Hydrated colloidal gel of dicalcium silicate}}{2CaO{\cdot}SiO_2{\cdot}xH_2O}$$

$Ca(OH)_2$ needles formed in step (2) gets studded in hydrated colloidal gel ($2CaO{\cdot}SiO_2{\cdot}xH_2O$) and thus impart strength to it.

   b. $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ gets hydrated to form colloidal gel ($3CaO{\cdot}Al_2O_3{\cdot}6H_2O$). The gel slowly loses water partly due to evaporation and partly by forming hydrates. Thus, cement sets to a hard mass.

5.10 BIOLOGICAL IMPORTANCE OF MAGNESIUM AND CALCIUM

Chemistry of life involves many chemical elements, magnesium and calcium are those elements which play an important role in biological processes. An adult body contains about 25 g of magnesium and 1200 g of calcium compared with only 5 g of iron and 0.06 g of copper. The daily requirement of calcium and magnesium is 200–300 mg. Magnesium ions are concentrated in the body fluids outside the cell, just in the same way as potassium ions concentrate inside the cell and sodium ions outside.

Magnesium ions catalyse a number of enzymatic reaction. Energy is stored in living beings in the form of phosphate linkages in adenosines phosphate (ATP). The formation of these linkages, i.e. storage of energy is catalysed by magnesium ions. Conversely, hydrolysis of phosphate linkages is accompanied by release of energy and this process is also catalysed by magnesium ions.

If the diet is rich in phosphate ions, magnesium may precipitate out as magnesium phosphate, $Mg_3(PO_4)_2$. This most commonly occurs in infections of urinary tract.

Chlorophyll, a green colouring pigment in plants which absorbs light and is essential for photosynthesis, contains magnesium ion, Mg^{2+}.

Calcium is also an essential element for all organisms. About 99% of the body calcium is present in bones and teeth apatite, $Ca_3(PO_4)_2$, and the enamel on teeth as fluoroapatite $[3Ca_3(PO_4)_2{\cdot}CaF_2]$. Calcium is required to trigger the contraction of muscles to maintain the regular heart beat and in blood clotting. The concentration of calcium in blood plasma is ~100 mg L^{-1} and it is maintained by two hormones namely, *calcitonin* and *parathyroid*. Bone is not an inert and unchanging substance. Calcium in bones are continuously dissolving into and redepositing from the blood plasma to the extent of ~400 mg daily in human beings. In normal adults, this exchange is in balance, but in women and elderly people, there is sometimes net loss of bone calcium, leading to the disease called osteoporosis. Calcium deficiency is caused due to actual absorption. One major difficulty is the tendency for calcium to be precipitated by a large number of anions present in food. In this regard, phosphate ion interferes to the greatest extent. Therefore, a protein-rich diet, which is rich in phosphates will be unfavourable for calcium absorption.

ILLUSTRATION 5.13

a. Give an example of laboratory desiccant.
b. What are the products formed when $MgCl_2{\cdot}6H_2O$ is heated?

Sol.

a. Anhydrous $CaCl_2$.
b. $MgCl_2{\cdot}6H_2O \xrightarrow{\Delta} MgO + 2HCl + 5H_2O$

ILLUSTRATION 5.14

Plaster of Paris on losing water and gaining water gives A and B. Identify A and B.

Sol. Plaster of Paris is $CaSO_4 \cdot \frac{1}{2}H_2O$

On losing water, it forms $CaSO_4$

$$CaSO_4 \cdot \frac{1}{2}H_2O \longrightarrow \underset{\text{(A) Dead burn plaster}}{CaSO_4} + \frac{1}{2}H_2O$$

On gaining water, it forms $CaSO_4{\cdot}2H_2O$

$$CaSO_4 \cdot \frac{1}{2}H_2O + \frac{3}{2}H_2O \longrightarrow \underset{\text{(B) Gypsum}}{CaSO_4.2H_2O}$$

(A) and (B) are $CaSO_4$ and $CaSO_4{\cdot}2H_2O$ respectively.

ILLUSTRATION 5.15

BaO_2 is a peroxide, but PbO_2 is not a peroxide. Why?

Sol. Metallic oxides which on treatment with dilute acids produce hydrogen peroxide are called peroxides. All peroxides contain a peroxide ion (O_2^{2-}) having the structure $[O–O]^{2-}$. PbO_2 does not contain peroxide ion and hence it cannot be called a peroxide.

ILLUSTRATION 5.16

Which is the weakest base among NaOH, $Ca(OH)_2$, KOH and $Be(OH)_2$.

Sol. $Be(OH)_2$ is the weakest base, since alkali metal hydroxides are stronger base than alkaline earth metal hydroxides. Also, basic character of hydroxides increases on moving down the group. Hence, $Be(OH)_2$ is the weakest base.

ILLUSTRATION 5.17

a. Why sodium chloride is added during electrolysis of fused anhydrous magnesium chloride?
b. Why magnesium oxide is used for the lining of steel making furnace?

Sol.

a. Sodium chloride (NaCl) is added to lower the fusion temperature of magnesium chloride ($MgCl_2$) and to make the mixture as a good conductor of electricity.

b. MgO is used for the lining of steel making furnace as it forms slag with the impurities and thus helps in removing them from iron.

ILLUSTRATION 5.18

Give the names and formula of the compounds indicated in the following statements.

a. A compound of Ca used in setting fractured bones.

b. A compound of calcium and hydrogen which is used as a portable source of hydrogen for filling balloons.

c. A compound of Ca, O, Cl and H used as germicide.

d. A compound of Mg, O, Cl and H used as a cement for joining cracked teeth.

e. A compound of Mg, Cl and O used as a drying agent.

f. A compound of Ca and O which when heated in oxycoal gas flame gives limelight.

g. A compound of Ca, C and N used as a fertiliser.

h. A triatomic compound of Ca which gives H_2 on treatment with water.

Sol.

a. Plaster of Paris, $CaSO_4 \cdot \frac{1}{2} H_2O$

b. Calcium hydride, CaH_2 (Hydrolith)

c. Bleaching powder, $CaOCl_2 \cdot H_2O$

d. Sorel cement, $MgCl_2 \cdot 5MgO \cdot xH_2O$

e. Anhydrone, Mg $(ClO_4)_2$

It has strong affinity for water giving $Mg(ClO_4)_2 \cdot 6H_2O$. It loses all six water molecules of crystallisation at 250°C and drying property is regenerated.

f. Calcium oxide, CaO

g. Calcium cyanamide, $CaCN_2$ (nitrolim)

h. Calcium hydride, CaH_2

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

ILLUSTRATION 5.19

a. What is the hybrid state of Be in $BeCl_2$ in vapour state. What will be the change in the hybrid state of $BeCl_2$ in the solid sate?

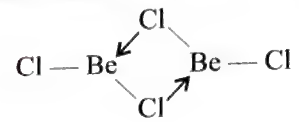
b. Draw the structure of (i) $BeCl_2$ (vapour state) and (ii) $BeCl_2$ (solid state).

c. Why do halides and hydrides of beryllium polymerise?

Sol.

a. In the vapour state, $BeCl_2$ exists as a linear molecule, i.e. each Be is bonded to two Cl atoms and Be is sp hybridised. Whereas in the solid state, $BeCl_2$ exists as a polymer and each Be is bonded to two Cl atoms by covalent bond and two Cl atoms by coordinate bond. Be atom in solid $BeCl_2$ is sp^3 hybridised.

b. In vapour state, $BeCl_2$ has chlorobridged dimer structure which dissociates into linear monomer at 1000°C.

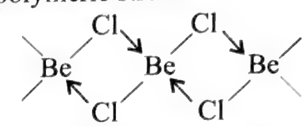


(Dimer)

Cl — Be — Cl

(Monomer)

Solid $BeCl_2$ has polymeric structure



c. The monomer BeH_2 and $BeCl_2$ formed with normal covalent bonds will result in only four electrons in the valence shell of beryllium and thus they are electron- deficient compounds. By polymerising, each atom shares its electrons with several neighbours and receives a share in their electron making the situation more favourable. Therefore, the hydrides and halides of Be polymerise.

CONCEPT APPLICATION EXERCISE 5.1

1. Name an element which is invariably bivalent and whose oxide is soluble in excess of NaOH and its dipositive ion has a noble gas core.
2. Differentiate between

   a. quicklime **b.** limewater **c.** slaked lime
3. How is plaster of Paris prepared? Describe its chief property due to which it is widely used.
4. Give reason for, '$NaHCO_3$ is known in solid state but $Ca(HCO_3)_2$ is not isolated in solid state.'
5. Contrast the action of heat on the following with reason:

   a. Na_2CO_3 and $CaCO_3$

   b. $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$

   c. $Ca(NO_3)_2$ and $NaNO_3$
6. Complete the following equations for the reaction between

   a. $Ca + H_2O$ **b.** $Ca(OH)_2 + Cl_2$

   c. $BeO + NaOH$ **d.** $BeO_2 + H_2SO_4$
7. The enthalpy of formation of hypothetical $CaCl_{(s)}$ theoretically found to be -188 kJ mol^{-1} and the $\Delta_f H^\ominus$ for $CaCl_{2(s)}$ is -795 kJ mol^{-1}. Calculate the $\Delta_f H^\ominus$ for the disproportionation reaction.

   $$2\,CaCl_{(s)} \longrightarrow CaCl_{2(s)} + Ca_{(s)}$$
8. Compare and contrast the chemistry of group 1 metals with that of group 2 metals with respect to

   a. Nature of oxides

   b. Solubility and thermal stability of carbonates

   c. Polarising power of cations

   d. Reactivity and reducing power
9. Mention the main constitutes of Portland cement.

What happens when:
  a. Magnesium is burnt in air
  b. Quicklime is heated with silica
  c. Chlorine reacts with slaked lime
  d. Calcium nitrate is heated

Describe two important uses of each of the following:
  a. Caustic soda
  b. Sodium carbonate
  c. Quicklime

List the raw materials required in the manufacture of Portland cement. What is the role of gypsum in it?

Like lithium in group 1, beryllium shows anomalous behaviour in group 2. Write three such properties of beryllium which make it anomalous in the group.

Beryllium exhibits some similarities with aluminium. Point out three such properties.

Name the chief forms of occurrence of magnesium in nature. How is magnesium extracted from one of its ores?

Commercial aluminium always contains some magnesium. Name two such alloys of aluminium. What properties are imparted by the addition of magnesium to these alloys?

Why is it that the *s*-block elements never occur free in nature? What are their usual modes of occurrence and how are they generally prepared?

How will you distinguish between:
  a. Magnesium and strontium
  b. K_2SO_4 and $BaSO_4$

Give reasons for the following:
  a. BeO is used as a refractory material.
  b. Beryllium halides are polymeric.
  c. $Be(OH)_2$ dissolves in NaOH, but $Ca(OH)_2$ does not.
  d. On hydrolysis at room temperature, Mg_3N_2 gives ammonia, whereas $MgCl_2$ gives HCl.

How is anhydrous magnesium chloride prepared from magnesium chloride hexahydrate?

Give reasons for the following:
  a. Why is calcium preferred over sodium to remove last traces of alcohol?
  b. A piece of buring magnesium ribbon continues to burn in SO_2.
  c. Halides of Be are soluble in organic solvents, while those of Ba are insoluble.
  d. $BeCl_2$ fumes in moist air, but other alkaline earth metal chlorides do not.

Lattice enthalpies of BeF_2, MgF_2, CaF_2 and BaF_2 are −2906, −2610, −2459 and −2367 kJ mol^{-1} respectively. Hydration enthalpies of Be^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+} and $F^{\ominus}$ are −2194, −1921, −1577, −130 and −457 kJ mol^{-1} respectively. Which of the fluorides has the highest solubility in water?

On treatment with cold water, an element (A) reacted quietly liberating a colourless, odourless gas (B) and a basic solution (C). Lithium reacted with (B) yielding a solid product (D) which effervesced with water to give a strongly basic solution (E) and gas (F). When CO_2 was bubbled through solution (C), initially a white ppt. (G) was formed, but this redissolved forming solution (H) when more CO_2 was passed, precipitate (G) effervesced when moistened with conc HCl and gave a brick red colouration to the Bunsen flame. When (G) was heated with carbon at 1000°C, a caustic white compound (I) was formed, which when heated with N_2 at 1000°C gave a solid (J) of some commercial importance. Identify (A) to (J) and explain the reactions.

24. Give reasons for the following:
  a. Anhydrous calcium sulphate (anhydrite) cannot be used as plaster of Paris.
  b. Limewater turns milky on passing CO_2 through it, but milkiness disappears on passing excess of CO_2.
  c. The reaction between marble and dil H_2SO_4 is not used to prepare CO_2.
  d. In the manufacture of Mg by carbon reduction of MgO, the product is cooled in the stream of an inert gas.
  e. Magnesium metal burns in air to give a white ash. When this ash is treated with water, the odour of ammonia can be detected.

25. What happens when:
  a. Water is added to CaC_2 and the resulting gas is passed through dil H_2SO_4 containing $HgSO_4$.
  b. Hydrated $MgCl_2$ is heated in presence of NH_4Cl.
  c. $FeCl_3$ solution is treated with Mg.
  d. NH_4Cl is heated with Mg.
  e. CO_2 is passed through limewater.
  f. SO_2 is passed through limewater.

26. Give the chemical formula of the following:

a. Plaster of Paris	**b.** Asbestos
c. Hydrolith	**d.** Lithopone
e. Gypsum	**f.** Marble
g. Anhydrite	**h.** Baryta water
i. Quicklime	**j.** Slaked lime
k. Magnesite	**l.** Kieserite
m. Epsom salt	**n.** Baryta
o. Beryl	**p.** Witherite
q. Celestine	**r.** Fluorspar

Solved Examples

EXAMPLE 5.1

Chemical (X) is used for water softening to remove temporary hardness. (X) reacts with sodium carbonate to generate caustic soda. When CO_2 is bubbled through (X)?

Sol. $Ca(OH)_2$ is used for water softening to remove temporary hardness.

$$\underset{(X)}{Ca(OH)_2} + CaHCO_3 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Ca(OH)_2 + Na_2CO_3 \longrightarrow \underset{\text{Sodium hydroxide or caustic soda}}{2NaOH} + CaCO_3$$

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{Milkiness}}{CaCO_3\downarrow} + H_2O$$

Hence, (X) is $Ca(OH)_2$.

EXAMPLE 5.2

Magnesium on heating in air gives (A) and (B). On reaction with water (B) gives a colourless gas (C). (C) when passed through $CuSO_4$ solution, gives a blue coloured solution (D). Identify (A), (B), (C) and (D).

Sol.

$$Mg + \text{air} \xrightarrow{\Delta} (A) + (B)$$

$$(B) \xrightarrow{H_2O} \underset{\text{Colourless gas}}{(C)}$$

$$\underset{\text{Blue coloured solution}}{(D)} \xleftarrow{CuSO_4 \text{ solution}} \underset{\text{Colourless gas}}{(C)}$$

Magnesium, Mg reacts with O_2 and N_2 present in the air to give

$$Mg + \underset{(\text{air})}{O_2} \xrightarrow{\Delta} MgO$$

$$Mg + \underset{(\text{air})}{N_2} \xrightarrow{\Delta} \underset{(B)}{Mg_3N_2}$$

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

Since on hydrolysis, Mg_3N_2 produces a colourless gas NH_3, (B) is Mg_3N_2, (A) is MgO and (C) is NH_3.

$$4NH_3 + CuSO_4 + H_2O \longrightarrow \underset{\text{(D) Blue coloured solution}}{[Cu(NH_3)_4]SO_4{\cdot}H_2O}$$

EXAMPLE 5.3

Thermal decomposition of a compound (X) yields, a basic oxide (Y) and an acidic oxide (Z) simultaneously. The acidic oxide (Z) can be absorbed by alkaline KOH. Indentify (X), (Y) and (Z).

Sol.

$$X \xrightarrow{\Delta} \underset{\text{Basic oxide}}{Y} + \underset{\text{Acidic oxide}}{Z}$$

$$\underset{(X)}{CaCO_3} \xrightarrow{\Delta} \underset{\text{Basic oxide (Y)}}{CaO} + \underset{\text{Acidic oxide (Z)}}{CO_2}$$

$$\underset{(Z)}{CO_2} + KOH \longrightarrow K_2CO_3 + H_2O$$

Hence (X), (Y) and (Z) are $CaCO_3$, CaO and CO_2 respectively.

EXAMPLE 5.4

$$\underset{\text{gypsum}}{CaSO_4{\cdot}2H_2O} \xrightarrow{200°C} (B) \xrightarrow{\text{Strong heating}} (C)$$

$$CaSO_4{\cdot}2H_2O \xrightarrow{120°C} (A)$$

Identify (A), (B) and (C).

Sol.

$$\underset{\text{Gypsum}}{CaSO_4{\cdot}2H_2O} \xrightarrow{120°C} \underset{\text{(A) Plaster of Paris}}{CaSO_4{\cdot}\frac{1}{2}H_2O} + \frac{3}{2}H_2O$$

$$CaSO_4{\cdot}2H_2O \xrightarrow{200°C} \underset{\substack{(B)\\ \text{Dead burnt plaster}}}{CaSO_4} + 2H_2O$$

$$CaSO_4 \xrightarrow{\text{Strong heating}} \underset{\substack{(C)\\ \text{Lime}}}{CaO} + SO_2 + O_2$$

Hence, (A) is plaster of Paris, $CaSO_4{\cdot}\frac{1}{2}H_2O$, (B) is dead burnt plaster, $CaSO_4$ and (C) is lime, CaO.

EXAMPLE 5.5

When a colourless gas (A), which is poisonous and burns with blue flame, is passed through aqueous NaOH solution, gives a compound (B). Compound (B) on heating gives (C). (C) gives a white precipitate (D) with $CaCl_2$. Both (C) and (D) decolourises $KMnO_4$. Identify (A) to (D).

Sol.

$$\underset{\text{Colourless, poisonous gas burns with blue flame}}{(A)} \xrightarrow{+\text{ NaOH soln}} (B)$$

$$(B) \xrightarrow{\Delta} (C)$$

$$(C) + CaCl_2 \longrightarrow \underset{\text{White ppt.}}{(D)}$$

(C) and (D) decolourise $KMnO_4$, this indicates that both are reducing agents.

(A) is CO, i.e. carbon monoxide which burns with blue flame and is poisonous.

$$\underset{(A)}{CO} + NaOH \longrightarrow \underset{\substack{\text{Sodium formate}\\ (B)}}{HCOONa}$$

$$2\,HCOONa \xrightarrow{\Delta} \underset{\substack{(C)\\ \text{Sodium oxalate}}}{\begin{matrix} COONa \\ | \\ COONa \end{matrix}} + H_2$$

$$\begin{matrix} COONa \\ | \\ COONa \end{matrix} + CaCl_2 \longrightarrow \underset{(D)}{\begin{matrix} COOCa \\ | \\ COOCa \end{matrix}} + 2NaCl$$

Both (C) and (D) decolourise $KMnO_4$, as the $MnO_4^{\ominus}$ ion is reduced to Mn^{2+}, a colourless species.

$$\left[\begin{matrix} COO^{\ominus} \\ | \\ COO^{\ominus} \end{matrix} \longrightarrow 2CO_2 + 2e^{\ominus}\right] \times 5$$

$$\left[MnO_4^{\ominus} + 5e^{\ominus} + 8H^{\oplus} \longrightarrow Mn^{2+} + 4H_2O\right] \times 2$$

$$5\begin{matrix} COO^{\ominus} \\ | \\ COO^{\ominus} \end{matrix} + 2MnO_4^{\ominus} + 16H^{\oplus} \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

Hence, (A) is CO, (B) is HCOONa, (C) is $\begin{matrix} COONa \\ | \\ COONa \end{matrix}$ and (D) is $\begin{matrix} COOCa \\ | \\ COOCa \end{matrix}$

EXAMPLE 5.6

An element (A) of group 2 gives brick red colour in the Bunsen flame. (A) burns in nitrogen atmosphere to give (B), which gets hydrolysed to produce gas (C) and an alkaline solution (D). The solution (D) on exposure to air produces a thin solid layer (E) on the surface. Identify (A) to (E).

Sol. Given

$$\underset{\text{Group 2 element}}{(A)} + N_2 \longrightarrow (B)$$

(A) $\xrightarrow{\text{Flame test}}$ Brick red colouration

$$(B) \xrightarrow{H_2O} \underset{\text{Gas}}{(C)} + \underset{\text{Alkaline solution}}{(D)}$$

$$(D) \xrightarrow{\text{Air}} \underset{\text{Thin solid layer}}{(E)}$$

Since (A) gives brick red colouration in the Bunsen flame, (A) is calcium.

$$\underset{(A)}{3Ca} + N_2 \longrightarrow \underset{\text{(B) (Calcium nitride)}}{Ca_3N_2}$$

$$Ca_3N_2 + 6H_2O \longrightarrow \underset{(D)}{3Ca(OH)_2} + \underset{(C)}{2NH_3}$$

$$\underset{(D)}{Ca(OH)_2} + \underset{(Air)}{CO_2} \longrightarrow \underset{(E)}{CaCO_3} + H_2O$$

Hence, (A) is calcium (Ca), (B) is Ca_3N_2, (C) is NH_3, (D) is $Ca(OH)_2$ and (E) is $CaCO_3$.

EXAMPLE 5.7

Identify from (A) to J.

$$(A) \xrightarrow[\text{cold}]{H_2O} \underset{\text{colourless odourless}}{(B)\text{ (gas)}} + \underset{\text{solution}}{(C)}$$

$$(B) + Li \longrightarrow \underset{\text{solid}}{(D)} \xrightarrow[\text{with effervescence}]{H_2O} \underset{\text{basic solution}}{(E)} + \text{Gas}$$

$$(C) + CO_2 \longrightarrow \underset{\text{white ppt.}}{(F)} \xrightarrow[CO_2]{\text{excess}} (G)$$

$$(F) \xrightarrow[2000°C]{\text{Carbon}} (H) \xrightarrow{H_2O} \underset{\text{Gas}}{(I)} \xrightarrow{AgNO_3} \underset{\text{white ppt.}}{(J)}$$

Precipitate (F) effervesced when moistened with conc. HCl and give deep red colouration to a flame test.

Sol. Since (F) gives deep red colour to flame, it should be Ca.

$$\underset{(A)}{Ca} \xrightarrow{H_2O} \underset{(B)}{H_2} + \underset{(C)}{Ca(OH)_2} \xrightarrow{CO_2} \underset{(F)}{CaCO_3}$$

$$\underset{(F)}{CaCO_3} \xrightarrow[CO_2]{\text{Excess}} \underset{(G)}{Ca(HCO_3)_2}$$

$$\underset{(F)}{CaCO_3} \xrightarrow[2000°C]{\text{Carbon}} \underset{(H)}{CaC_2}$$

$$\underset{(B)}{H_2} \xrightarrow[\Delta]{Li} \underset{(D)}{LiH} \xrightarrow{H_2O} \underset{\text{(E) Basic solution}}{LiOH} + H_2\text{ (gas)}$$

EXAMPLE 5.8

Identify P, Q, R and S.

$$\text{Calcium imide} \xrightarrow{H_2O} Q + R\text{ (Gas)}$$

$$R \xrightarrow{\text{Bleaching powder}} \ldots$$

$$3Mg(OH)_2 + R(Gas) \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Mg/\Delta} S(Gas) + 3CaCl_2 + 3H_2O$$

Sol.

(i) $\underset{(P)}{Ca(NH)} + 2H_2O \longrightarrow \underset{(Q)}{Ca(OH)_2} + \underset{(R)}{NH_3(g)}$

(ii) $\underset{(R)}{2NH_3} + \underset{\text{Bleaching powder}}{3CaOCl_2} \longrightarrow \underset{(S)}{N_2(g)} + 3CaCl_2 + 3H_2O$

$$\underset{(S)}{N_2} \xrightarrow{3Mg/\Delta} Mg_3N_2 \xrightarrow{6H_2O} 3Mg(OH)_2 + \underset{(R)}{2NH_3}$$

Exercises

Single Correct Answer Type

General characteristics of Alkaline Earth Metals

1. Beryllium shows diagonal relationship with
(1) Mg (2) Na
(3) Al (4) B

2. Dolomite is mineral whose formula is
(1) $CaCO_3$ (2) $MgCO_3$
(3) $CaCO_3{\cdot}MgCO_3$ (4) $CaSO_4{\cdot}2H_2O$

3. The ionisation enthalpy of alkaline earth metals is
(1) Greater than alkali metals but less than elements of group 13
(2) Less than alkali metals
(3) Greater than elements of groups 1 and 13
(4) Equal to alkali metals

4. Out of the following metals that cannot be obtained by electrolysis of the aqueous solution of their salts is
(1) Ag (2) Mg
(3) Cu (4) Au

5. An important ore of magnesium is
(1) Malachite (2) Cassiterite
(3) Carnallite (4) Galena

6. Calcium is obtained by the
(1) Roasting of limestone
(2) Electrolysis of a solution of calcium chloride in water
(3) Reduction of calcium chloride with carbon
(4) Electrolysis of molten anhydrous calcium chloride

7. Which of the following compound is most soluble in water?
(1) $MgSO_4$ (2) $CaSO_4$
(3) $SrSO_4$ (4) $BaSO_4$

8. Ca^{2+} is isoelectronic with
(1) Mg^{2+} (2) Kr
(3) Ar (4) $Na^{\oplus}$

9. Which of the following electronic configurations in the outermost two shells is characteristic of the alkaline earth metals?
(1) $(n-1)\,s^2p^6ns^2$ (2) $(n-1)\,s^2p^6d^{10}ns^2$
(3) $(n-1)\,s^2p^6ns^2p^1$ (4) None of these

10. Magnesium combines with nitrogen to form a nitride, which reacts with water to form a colourless gas. The gas is
(1) NH_3 (2) N_2O
(3) NO (4) N_2O

11. Which has the highest electronegativity?
(1) Li (2) Be
(3) Mg (4) Na

12. Which of the following undergoes disproportionation?
(1) Ba^{2+} (2) $Ba^{\oplus}$
(3) BaH_2 (4) $BaSO_4$

13. Which of the following alkaline earth metal oxide is most basic?
(1) BeO (2) MgO
(3) CaO (4) BaO

14. Which of the following metal reacts with cold H_2O with the evolution of H_2 gas?
(1) Ca (2) Al
(3) Zn (4) Cu

15. Which of the following salt will give a green colour in fire works?
(1) Ca (2) Ba
(3) Mg (4) Sr

16. Which of the following does not contain the true peroxide ion?
(1) Na_2O_2 (2) H_2O_2
(3) BaO_2 (4) SrO_2

17. The most abundant alkaline earth metal in the earth's crust is
(1) Be (2) Mg
(3) Ca (4) Sr

18. The hydration enthalpy of Mg^{2+} is greater than
(1) Al^{3+} (2) $Na^{\oplus}$
(3) Ca^{2+} (4) Sr^{2+}

19. Which of the following metal is the most difficult to extract from its oxide?
(1) Cs (2) Ca
(3) Mg (4) Ag

20. The most probable reason that the alkaline earth metals give dipositive ions instead of unipositive ion is
(1) The compounds with +2 oxidation state have more lattice enthalpy than those with +1 oxidation state.
(2) The values of their first and second ionisation potentials are not very much different.
(3) The dipositive ion has grater charge than the unipositive ion.
(4) The compounds of +1 oxidation state of these metals are not stable.

21. Typical elements is the name given to the elements of
(1) Zero group (2) Group 2
(3) 2nd and 3rd period (4) Group 1

22. Two metals (A) and (B) belong to the same group of the periodic table. Metal (A) forms an insoluble oxide but a soluble sulphate, metal (B) forms a soluble oxide but an insoluble sulphate. Both metals (A) and (B) form hydroxides which are soluble in alkalis. (A) and (B) are
(1) Ba and Mg (2) Na and K
(3) Mg and Ba (4) K and Rb

23. Which of the following forms covalent compound?
(1) Be (2) Mg
(3) Ca (4) Sr

24. The compounds of alkaline earth metals have the following magnetic nature:
(1) Diamagnetic (2) Antiferromagnetic
(3) Ferromagnetic (4) Paramagnetic

25. As the nuclear charge increases from neon to calcium, the orbital energies
(1) Increase (2) Increases very rapidly
(3) Increase very slowly (4) Fall

26. Be and Al exhibit many properties which are similar. But the two elements differ in
(1) Forming covalent bonds
(2) Forming polymeric hydrides
(3) Exhibiting maximum covalency in compounds
(4) Exhibiting amphoteric nature in their oxides

27. Magnesium is an important component of which biomolecule occurring extensively in living world?
(1) Haemoglobin (2) ATP
(3) Chlorophyll (4) Vitamin B_{12}

28. Several blocks of magnesium are fixed to the bottom of a ship to
(1) Prevent action of water and salt
(2) Prevent puncturing by under sea rocks
(3) Keep away the sharks
(4) Make the ship lighter

29. A compound (A) gives brick red flame and breaks down on heating giving oxygen and brown gas. (A) is
(1) $CaCO_3$ (2) $MgCO_3$
(3) $Mg(NO_3)_2$ (4) $Ca(NO_3)_2$

30. Which of the following pair of substances give same gaseous product on reaction with water?
(1) Na and Na_2O_2 (2) Ba and BaO_2
(3) Ca and CaH_2 (4) Ca and CaO

31. An alkaline earth metal gives a salt with chlorine which is sparingly soluble in water at room temperature but fairly soluble in boiling water. It also forms a sulphate whose mixture with a sulphide of a transition metal is called 'lithopone' and is used as white pigment. The alkaline earth metal is
(1) Ca (2) Mg
(3) Sr (4) Ba

32. The metal that is extracted from sea water is
(1) Mg (2) Ca
(3) Be (4) Ba

33. The element which shows radioactivity is
(1) Mg (2) Sr
(3) Ba (4) Ra

34. Magnesium wire burns in the atmosphere of CO_2 because
(1) Magnesium acts as an oxidising agent
(2) Magnesium has two electrons in the outermost orbital
(3) Magnesium acts as a reducing agent and removes oxygen from CO_2
(4) None of the above

35. On strong heating of CaO and C, the products fromed are
(1) Ca and CO (2) CaC_2 and CO
(3) $Ca(OH)_2$ (4) CaC_2 and CO_2

36. The nature of the oxide of radium is
(1) Basic (2) Acidic
(3) Neutral (4) Amphoteric

37. Radium is obtained from
(1) Limestone (2) Rutile
(3) Pitchblende (4) Barytes

38. Which of the following is used for taking the X-ray spectra of the digestive system:
(1) $CaSO_4$ (2) $BaSO_4$
(3) $MgSO_4$ (4) $BaCO_3$

39. Among the given statements, the incorrect one is
(1) Be differs much from other alkali metals than Li does from other alkali metals.
(2) Be generally forms covalent compounds.
(3) Be forms a very strong complex, $[Be(H_2O)_4]^{2+}$.
(4) Be usually has more than four water of crystallisation associated with it.

40. Mg is precipitated and estimated gravimetrically as:
(1) $Mg(NH_4)PO_4$ (2) $Mg(NH_4)PO_4{\cdot}6H_2O$
(3) $Mg_2P_2O_7$ (4) $Mg_3(PO_4)_2$

41. Select the incorrect statements
(1) Thermal stability of $BaCO_3$ is more than that of $BeCO_3$
(2) BaO is more basic than BeO
(3) $BeSO_4$ is used in diagnosing stomach ulcers.
(4) *Ksp* value of $Ba(OH)_2$ is greater than that of $Be(OH)_2$

42. Select the incorrect statement
(1) Mg is used as a reducing agent in the extraction of boron and silicon.
(2) White pigment lithopone is $(BaS + ZnSO_4)$
(3) The order of hydration energy of the following is: $Al^{3+} > Be^{3+} > Mg^{3+} > Mg^{2+} > Na^{\oplus}$
(4) Alkaline earth metals are weaker reducing agent than alkali metals.

43. Select the correct statements
(1) Function of $CaCl_2$ in the electrolytic preparation of Na is raise the melting point of NaCl melt.
(2) Be shows a covalency beyond 4.
(3) $BeCl_2$ fumes in air.
(4) Dehydration of $MgCl{\cdot}6H_2O$ is carried out with H_2SO_4

44. Select the incorrect statements
(1) $Be(OH)_2$ dissolves in NaOH and forms sodium tetra hydroxidoberyllate.
(2) $Be(OH)_2$ dissolves in acid to form beryllium salt.
(3) Mg and C are produced when MgO reacts with CaC_2
(4) Melting point of CaF_2 is lower than that of CaI_2

Compounds of Alkaline Earth Metals

45. Formula of gypsum salt is
(1) $CaSO_4 \cdot 2H_2O$ (2) $CaSO_4 \cdot \frac{1}{2} H_2O$
(3) $2CaSO_4 \cdot H_2O$ (4) $CaSiO_3$

46. CaC_2 reacts with water to give
(1) Methane (2) Ethane
(3) Ethylene (4) Acetylene

47. Plaster of Paris is
(1) $CaSO_4 \cdot \frac{1}{2} H_2O$ (2) $CaSO_4 \cdot 2H_2O$
(3) $CaSO_4 \cdot CaCO_3$ (4) $CaSO_4 \cdot 5H_2O$

48. Mixture of $CaCN_2$ and C is called
(1) Barytes (2) Anhydrite
(3) Nitrolim (4) Iceland spar

49. Lithopone is a mixture of
(1) $BaSO_4$ and BaS (2) $BaSO_4$ and ZnS
(3) BaO and ZnS (4) $BaCO_3$ and ZnO

50. Slaked lime is obtained when water is added to
(1) $CaSO_4 \cdot \frac{1}{2} H_2O$ (2) $CaCl_2$
(3) CaO (4) $CaCO_3$

51. Which of the following is not present in cement?
(1) Gypsum (2) Clay
(3) Alumina (4) Alum

52. Gypsum on heating to 390 K gives
(1) $CaSO_4 \cdot 2H_2O$ (2) $CaSO_4$
(3) $CaSO_4 \cdot \frac{1}{2} H_2O$ (4) SO_3 and CaO

53. Ripening of fruits can be carried out in presence of
(1) Na_2SO_4 (2) NaCl
(3) $CaCl_2$ (4) CaC_2

54. The drying agent which absorbs carbon dioxide and reacts violently with water is
(1) Sodium carbonate (2) Alcohol
(3) Conc H_2SO_4 (4) Calcium oxide

55. The difference of number of water molecules in gypsum and plaster of Paris is
(1) $\frac{5}{1}$ (2) 2
(3) 1/2 (4) $1\frac{1}{2}$

56. Which of the following decomposes at highest temperature?
(1) $SrCO_3$ (2) $BaCO_3$
(3) $CaCO_3$ (4) $MgCO_3$

57. When a substance A reacts with water it produces a combustible gas B and a solution of substance C in water. When another substance D reacts with this soution of C, it also produces the same gas B on warming but D can produce B on reaction with dilute sulphuric acid at room temperature. A imparts a golden yellow colour to a smokeless flame of Bunsen flame. A, B, C and D are respectively.
(1) K, H_2, KOH, Al (2) Na, H_2, NaOH, Zn
(3) CaC_2, C_2H_2, $Ca(OH)_2$, Fe (4) Ca, H_2, $Ca(OH)_2$, Sn

58. The basic strength of which hydroxide is maximum
(1) LiOH (2) NaOH
(3) $Ca(OH)_2$ (4) KOH

59. Of the following, an amphoteric hydroxide is
(1) $Ca(OH)_2$ (2) NaOH
(3) $Be(OH)_2$ (4) LiOH

60. The following compounds have been arranged in order of their increasing stabilities. Identify the correct order.
K_2CO_3(I) $MgCO_3$(II)
$CaCO_3$(III) $BeCO_3$(IV)
(1) I < II < III < IV (2) IV < II < III < I
(3) IV < II < I < III (4) II < IV < III < I

61. Which of the following is insoluble in acetic acid?
(1) $CaCO_3$ (2) CaC_2O_4
(3) $Ca(OH)_2$ (4) CaO

62. Which of the following fluoride is more soluble in water?
(1) BaF_2 (2) BeF_2
(3) MgF_2 (4) CaF_2

63. Solubility of alkaline earth metal carbonates in water is as follows:
(1) $BeCO_3 > MgCO_3 > CaCO_3 > BaCO_3$
(2) $BeCO_3 > CaCO_3 > MgCO_3 > BaCO_3$
(3) $BeCO_3 < MgCO_3 < CaCO_3 < BaCO_3$
(4) $BaCO_3 < BeCO_3 < MgCO_3 < CaCO_3$

64. Epsom salt is
(1) $MgSO_4 \cdot 7H_2O$ (2) $CaSO_4 \cdot 2H_2O$
(3) $CaSO_4$ (4) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

65. Which of the following alkaline earth metal carbonate is thermally least stable?
(1) $BeCO_3$ (2) $CaCO_3$
(3) $MgCO_3$ (4) $BaCO_3$

66. The basic character of the alkaline earth metal hydroxides is as follows:
(1) $Mg(OH)_2 > Ba(OH)_2 > Ca(OH)_2 > Sr(OH)_2$
(2) $Be(OH)_2 > Sr(OH)_2 > Ca(OH)_2 > Mg(OH)_2$
(3) $Sr(OH)_2 > Ca(OH)_2 > Ba(OH)_2 > Mg(OH)_2$
(4) $Mg(OH)_2 > Ba(OH)_2 > Sr(OH)_2 > Ca(OH)_2$

67. Which of the following bicarbonate is insoluble in water?
(1) $Mg(HCO_3)_2$ (2) $NaHCO_3$
(3) $KHCO_3$ (4) $Ca(HCO_3)_2$

68. The oxidation state of the most electronegative elements in the products of the reaction of BaO_2 with dil H_2SO_4 are
(1) 0 and –1 (2) –1 and –2
(3) –2 and 0 (4) – 2 and +1

69. Anhydrous $MgCl_2$ is obtained by heating hydrated salt, $MgCl_2 \cdot 6H_2O$.

(1) Strongly in air
(2) In presence of coke
(3) In presence of conc H_2SO_4 which absorbs moisture
(4) In presence of dry HCl gas

70. Which of the following is used as an antacid?
(1) MgO (2) $Mg(OH)_2$
(3) $MgSO_4$ (4) $MgCO_3$

71. Na_2SO_4 is soluble in water whereas $BaSO_4$ is sparingly soluble because
(1) The lattice enthalpy of Na_2SO_4 is less than its hydration enthalpy.
(2) Sodium is monovalent ion whereas barium is a divalent ion.
(3) The hydration enthalpy of sodium sulphate is less than its lattice enthalpy.
(4) The lattice enthalpy of barium sulphate is less than its hydration enthalpy.

72. Mg burns in air to give
(1) Mg_3N_2 (2) MgO
(3) MgO and Mg_3N_2 (4) $MgCO_3$

73. Which of the following is decomposed on heating?
(1) Na_2CO_3 (2) $MgCO_3$
(3) K_2CO_3 (4) Pb_2CO_3

74. For two ionic solids, CaO and KI, which of the following statement is false?
(1) Lattice enthalpy of CaO is much higher than that of KI.
(2) CaO has high melting point.
(3) KI has low melting point.
(4) KI is soluble in benzene.

75. Which of the following substance can be used for drying neutral or basic gases?
(1) Na_2CO_3 (2) $CaCO_3$
(3) CaO (4) Na_2CO_3

76. Which one is the active constituent of bleaching powder?
(1) Ca(OCl)Cl (2) $Ca(OCl)_2$
(3) $Ca(ClO_2)_2$ (4) $Ca(ClO_2)Cl$

77. Bleaching powder loses its power on keeping for a long time because
(1) It absorbs moisture
(2) It changes into calcium hypochlorite
(3) It changes into calcium chloride and calcium chlorate
(4) It changes into calcium chloride and calcium hydroxide

78. A sodium salt of unknown anion when treated with $MgCl_2$ gives a white ppt. on boiling. The anion is
(1) $HCO_3^{\ominus}$ (2) CO_3^{2-}
(3) SO_4^{2-} (4) $NO_3^{\ominus}$

79. Which of the following on thermal decomposition yields a basic as well as an acidic oxide?
(1) $KClO_3$ (2) Na_2CO_3
(3) $NaNO_3$ (4) $CaCO_3$

80. The substance not likely to contain $CaCO_3$ is
(1) Dolomite (2) A marble statue
(3) Calcined gypsum (4) Sea shells

81. One mole of magnesium nitride on reaction with an excess of water gives
(1) One mole of NH_3 (2) Two moles of NH_3
(3) One mole of HNO_3 (4) Two moles of HNO_3

82. The name and formula of the compound of magnesium, chlorine and oxygen used as a drying agent is
(1) Magnesium oxychlorite, $Mg(OCl)_2$
(2) Magnesium chlorate, $Mg(ClO_3)_2$
(3) Magnesium perchlorate, $Mg(ClO_4)_2$
(4) None of the above

83. Salt used as a purgative is
(1) NaCl (2) $MgCl_2{\cdot}6H_2O$
(3) $MgSO_4{\cdot}7H_2O$ (4) $Ca_3Al_2O_6$

84. Silica reacts with magnesium to form magnesium compound (X). (X) reacts with dilute HCl and forms (Y). (Y) is:
(1) MgO (2) $MgSiO_3$
(3) $SiCl_4$ (4) $MgCl_2$

85. Which of the following gives propyne on hydrolysis?
(1) Al_4C_3 (2) Mg_2C_3
(3) B_4C (4) La_4C_3

86. A metal X on heating in nitrogen gas gives Y. Y on treatment with H_2O gives a colourless gas which when passed through $CuSO_4$ solution gives a blue colour. Y is:
(1) $Mg(NO_3)_2$ (2) Mg_3N_2
(3) NH_3 (4) MgO

87. A metal M readily forms water soluble MSO_4, water insoluble $M(OH)_2$ and oxide MO which becomes inert on heating. The hydroxide is soluble in NaOH. Then M is:
(1) Be (2) Mg
(3) Ca (4) Sr

88. A sodium salt on treatment with $MgCl_2$ gives white precipitate on heating. The anion of the sodium salt is:
(1) CO_3^{2-} (2) $HCO_3^{\ominus}$
(3) SO_4^{2-} (4) $NO_3^{\ominus}$

89. Select the incorrect statement
(1) Polymeric $(BeCl_2)_n$ contains three centre three electron bonds.
(2) $MgSO_4{\cdot}7H_2O$ is isomorphous with $ZnSO_4{\cdot}7H_2O$
(3) Be forms tetrahedral complexes eg, $[Be(C_2O_4)_2]^{2-}$
(4) Al forms $[AlF_6]^{3-}$ an octahedral complex.

90. Select the incorrect statement
(1) Milk of magnesia which is used as antacid, chemically is, $(MgCl_2 + MgO)$
(2) Mortar is a mixture of $Ca(OH)_2$, Silica and water.
(3) Plaster of Paris is $CaSO_4 \cdot \frac{1}{2}H_2O$
(4) Plaster of Paris when mixed with correct amount of water sets into a solid mass due to the formation of $CaSO_4{\cdot}2H_2O$.

91. Select the incorrect statement
(1) Mg_2C_3 reacts with H_2O forms propyne gas, C_3^{4-} ion contains 2σ-bond and 2π-bond
(2) Density of Mg is less than Ca
(3) Be, Sn and Ga are amphoteric metals.
(4) CaO_2 is more stable than MgO_2

92. Select the incorrect statements
(1) $Ca_3(PO_4)_2$ can be used directly as fertilizer.
(2) Li_2SO_4 does not form double salt like alum.
(3) $BeCl_2$ can be easily hydrolyzed
(4) $K^{\oplus}$ and $NH_4^{\oplus}$ ions have many similarities in their test

93. Select the incorrect statement
(1) Li reacts with NH_3 to form $LiNH_2$
(2) Mg gets oxidized, when heated in CO_2 atmosphere
(3) Be and Mg do not dissolve in liquid NH_3
(4) BeF_2 forms complex ion with NaF

Multiple Correct Answers Type

General characteristics of alkaline earth metals

1. Which of the following is/are example(s) of diagonal pairs?
(1) Li and Na (2) Li and Be
(3) Li and Mg (4) Be and Al

2. Which of the following elements form peroxides when heated in excess of air?
(1) K (2) Na
(3) Ba (4) Ca

3. The alkaline earth metals forming ionic oxides are
(1) BeO (2) MgO
(3) CaO (4) SrO

4. Which of the following metals dissolve in liquid ammonia?
(1) Sr (2) Ca
(3) Ba (4) Be

5. Which of the following properties show a reverse trend in moving down the group of alkali and alkaline earth metals?
(1) Solubility of hydroxides (2) Solubility of carbonates
(3) Solubility of sulphates (4) Solubility of oxides

6. Which of the following statement (s) is/are not true about the diagonal relationship of Be and Al?
(1) Their oxides are basic
(2) They become passive by conc HNO_3
(3) Both react with NaOH to liberate hydrogen
(4) Their carbides give acetylene on hydrolysis

7. The hydration enthalpy of Mg^{2+} ion is higher than that of
(1) Al^{3+} (2) Be^{2+}
(3) $Na^{\oplus}$ (4) $K^{\oplus}$

8. Which among the following has the tendency to form covalent compounds?
(1) Li (2) Be
(3) Sr (4) Mg

9. Select the correct statements about barium:
(1) It shows photoelectric effect.
(2) It is silvery white metal.
(3) It forms $Ba(NO_3)_2$ which is used in preparation of green fire.
(4) Its ionisation enthalpy is less than radium.

10. Which of the following oxides have rock salt structure with coordination number 6:6?
(1) BeO (2) MgO
(3) CaO (4) SrO

11. Mg and Zn have the following resemblance:
(1) MgO and ZnO are amphoteric.
(2) $MgCO_3$ and $ZnCO_3$ both on heating give corresponding oxide.
(3) Both are used as electrodes.
(4) Both are used to prevent corrosion.

12. Be and Al have the following resemblance due to diagonal relationship:
(1) Have nearly equal electronegativity
(2) Form amphoteric oxides
(3) Have same charge/radius ratio
(4) Both form dimeric halides

13. Which of the following metal(s) do(es) not give characteristic flame colouration?
(1) Ca (2) Mg
(3) Be (4) Na

14. Dolomite is a mineral of
(1) Aluminium (2) Magnesium
(3) Calcium (4) Potassium

15. Select the incorrect statements
(1) Generally IE_1 of 1st group elements < IE_1 of 2nd group elements
(2) Generally solubilities of sulphates of 1st group elements is greater than that of 2nd group sulphates
(3) Be reacts with steam to give $Be(OH)_2$
(4) Mg is extracted by the oxidation of MgO

Compounds of alkaline earth metals

16. Soduim sulphate is soluble in water but barium sulphate is sparingly soluble because
(1) The hydration enthalpy of Na_2SO_4 is more than its lattice enthalpy.
(2) The lattice enthalpy of $BaSO_4$ is more than its hydration enthalpy.
(3) The lattice enthalpy has no role to play in solubility.
(4) The lattice enthalpy of Na_2SO_4 is more than its hydration enthalpy.

17. Which of the following statements are false?
(1) $BeCl_2$ exists as dimer in the vapour state and polymeric in the solid state.
(2) Calcium hydride is called hydrolith.
(3) The oxides of Be and Ca are amphoteric.
(4) Bicarbonates of Na and Sr are insoluble in water.

18. Which of the following groups of elements have properties that are most similar?
(1) Na, K, Cs
(2) Mg, Sr, Ba
(3) Be, Al, Ca
(4) Be, Ra, Cs

19. Magnesium burns in the atmosphere of the following gases?
(1) CO_2
(2) N_2O
(3) N_2
(4) SO_2

20. In which of the following, hydration enthalpy is greater than the lattice enthalpy?
(1) $BaSO_4$
(2) $BaCO_3$
(3) Na_2SO_4
(4) Na_2CO_3

21. Yellow phosphorous on reaction with $Ca(OH)_2$ gives:
(1) $Ca(H_2PO_4)_2$
(2) $Ca(H_2PO_2)_2$
(3) PH_3
(4) PH_5

22. Which of the following pairs can be distinguished by the action of heat?
(1) Na_2CO_3 and $CaCO_3$
(2) K_2CO_3 and $MgCO_3$
(3) $Ca(NO_3)_2$ and $NaNO_3$
(4) $MgCl_2{\cdot}6H_2O$ and $CaCl_2{\cdot}6H_2O$

23. Identify the correct statement(s):
(1) Gypsum contains a lower percentage of calcium than plaster of Paris.
(2) Gypsum is $CaSO_4{\cdot}2H_2O$.
(3) Plaster of Paris is obtained by hydration of gypsum.
(4) Gypsum is obtained by hydration of plaster of Paris.

24. The correct statement(s) is/are
(1) $BeCl_2$ is a covalent compound
(2) $BeCl_2$ can form dimer
(3) $BeCl_2$ is an electron-deficient molecule
(4) The hybrid state of Be in $BeCl_2$ is sp^2

25. Gypsum on heating gives
(1) $CaSO_4{\cdot}\frac{1}{2}H_2O$
(2) $CaSO_4$
(3) $CaO + SO_3$
(4) $CaS + O_2$

26. Mg^{2+} can be detected and estimated in hard water by titrating with EDTA at pH = 10 using $NH_4OH + NH_4Cl$ buffer. The end point is given by the apearance of blue colour. The indicator used is
(1) Solochrome black
(2) Eriochrome black T
(3) Eosin
(4) Bromophenol

27. Select the **correct** statements
(1) $MgCl_2.6H_2O$ on reaction with $(Na_2HPO_4 + NH_4OH)$ gives $Mg(NH_4)PO_4$
(2) The anhydrous $CaSO_4$ is called gypsum.
(3) $Na_2S_2O_3$ is used as meat preservative.
(4) $CaSO_4$ on heating at 125°C gives $(CaSO_4)_2H_2O$

28. Select the correct statements
(1) Bicarbonates salt of alkaline earth metals and $Zn(HCO_3)_2$ and $Ag(HCO_3)$ exist in solid state.
(2) Ionic size of following is:
$P^{3-} > S^{2-} > K^{\oplus} > C^{+2}$
(3) Electric conductance of following in aqueous solution is:
$Na^{\oplus} > K^{\oplus} > Rb^{\oplus} > Cs^{\oplus}$
(4) Ionic mobilities of following in aqueous solution is:
$F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

29. Select the correct statements
(1) Sorel cement composition is $MgCl_2.5MgO.xH_2O$
(2) Xylotite is a weather proof material is obtained by mixing sorel cement with dust, cork waste etc.
(3) For good quality of sorel cement.
$$\frac{\% CaO}{\% SiO_2 + \% Al_2O_3 + \% Fe_2O_3} = 2.$$
(4) For good quality of sorel cement.
$$\frac{\% SiO_2}{\% Al_2O_3} = 2.5 \text{ to } 4.$$

Linked Comprehension Type

Paragraph 1

Solubility of an ionic compound in water is mainly dependent on:
(1) Lattice enthalpy (2) Hydration enthalpy

Both these factors oppose each other and the resultant of these determines the solubility of an ionic compound in water. If lattice enthalpy has greater value, the compound is less soluble. In case hydration enthalpy has greater value, the compound is highly soluble in water.

1. Compounds of alkaline earth metals are less soluble than alkali metals, due to:
(1) Their high hydration enthalpy
(2) Their high lattice enthalpy
(3) Their increased covalent character
(4) Their high ionisation enthalpy.

2. Which of the following is more soluble in water?
(1) $MgSO_4$
(2) $CaSO_4$
(3) $SrSO_4$
(4) $BaSO_4$

3. BeF_2 is soluble in water while fluorides of other alkaline earth metals are insoluble because of:
(1) Covalent nature of BeF_2
(2) Ionic nature of BeF_2
(3) Greater hydration enthalpy of Be^{2+} ion
(4) Greater lattice enthalpy of Be^{2+} ion

4. Which of the following is less soluble in water?
(1) $Mg(OH)_2$
(2) $Ca(OH)_2$
(3) $Sr(OH)_2$
(4) $Ba(OH)_2$

5. Compound is soluble in water if
(1) Hydration enthalpy is greater than lattice enthalpy
(2) Hydration enthalpy is less than lattice enthalpy
(3) Hydration enthalpy and lattice enthalpy are same
(4) None of the above

Paragraph 2

Alkali and alkaline earth metals have low ionisation enthalpies and hence exhibit characteristic flame colouration. They have high negative electrode potentials and hence are strong reducing agents. They dissolve in liquid ammonia to give a solution which conducts electricity and act as strong reducing agent. Being stronger reducing agent than hydrogen, they are usually prepared by the electrolysis of their fused chlorides. Their oxides are basic and the basic strength increases down the group. The solubility of carbonates and sulphates of alkali and alkaline earth metals show opposite trends. Only the carbonates of Li and alkaline earth metals decompose on heating. The bicarbonates of both alkali and alkaline earth metals on heating give carbonates.

6. Which of the following process is used in the extractive metallurgy of sodium?
   (1) Electrolysis of aqueous solution
   (2) Thermite reduction
   (3) Electrolysis of fused salt
   (4) Self-reduction

7. The correct decreasing order of basic character of the oxides is
   (1) $K_2O > MgO > SrO > Cs_2O$
   (2) $Cs_2O > K_2O > SrO > MgO$
   (3) $MgO > SrO > K_2O > Cs_2O$
   (4) $Cs_2O > K_2O > MgO > SrO$

8. Property of alkaline earth metals that increases with their atomic number is
   (1) Ionisation enthalpy
   (2) Solubility of their hydroxides
   (3) Solubility of their sulphates
   (4) Electronegativity

9. Identify the correct order of thermal stabilities.
   (1) $K_2CO_3 < MgCO_3 < CaCO_3 < BeCO_3$
   (2) $BeCO_3 < CaCO_3 < MgCO_3 < K_2CO_3$
   (3) $BeCO_3 < MgCO_3 < CaCO_3 < K_2CO_3$
   (4) $CaCO_3 < BeCO_3 < MgCO_3 < K_2CO_3$

10. The compound insoluble in acetic acid is
    (1) Calcium oxide (2) Calcium carbonate
    (3) Calcium oxalate (4) Calcium hydroxide

Paragraph 3

According to Fajans' rules, the percentage of covalent character in an ionic compound increases if the cation is highly charged or small in size and the anion is large or cation has pseudoinert gas configuration. As a result of the increased covalent character, solubility in less polar solvent increases and the melting point decreases.

11. Which of the following has the lowest melting point?
    (1) KCl (2) LiCl
    (3) CsCl (4) RbCl

12. The correct order of decreasing covalent character is
    (1) $LiCl > NaCl > BeCl_2$ (2) $BeCl_2 > LiCl > NaCl$
    (3) $NaCl > LiCl > BeCl_2$ (4) $BeCl_2 > NaCl > LiCl$

13. The correct order of increasing ionic character is
    (1) $NaCl < KCl < RbCl < CsCl$
    (2) $NaCl < KCl < CsCl < RbCl$
    (3) $KCl < NaCl < CsCl < RbCl$
    (4) $CsCl < RbCl < KCl < NaCl$

14. The correct order of increasing ionic character is
    (1) $BeCl_2 < MgCl_2 < CaCl_2 < BaCl_2$
    (2) $BeCl_2 < MgCl_2 < BaCl_2 < CaCl_2$
    (3) $BeCl_2 < BaCl_2 < MgCl_2 < CaCl_2$
    (4) $BaCl_2 < CaCl_2 < MgCl_2 < BeCl_2$

15. Which of the following has highest melting point?
    (1) LiCl (2) NaCl
    (3) KCl (4) RbCl

Paragraph 4

A compound (A) on heating in Bunsen flame imparts brick red colouration. (A) on heating gives CO_2 gas and a residue (B). The residue (B) when treated with water gives (C). On passing an excess of CO_2 through (C) in water, a clear solution (D) is obtained. On boiling (D), compound (A) is reformed.

16. Compound (A) is
    (1) $CaCO_3$ (2) $MgCO_3$
    (3) $SrCO_3$ (4) $BaCO_3$

17. Residue (B) is
    (1) CaO (2) CaO_2
    (3) SrO (4) BaO

18. Compound (C) is
    (1) $Ca(OH)_2$ (2) $Sr(OH)_2$
    (3) $Ba(OH)_2$ (4) $[Sr(H_2O)_6]^{2-}$

19. Compound (D) is
    (1) $Ca(HCO_3)_2$ (2) $Sr(HCO_3)_2$
    (3) $Ba(HCO_3)_2$ (4) $Ca(OH)_2$

Paragraph 5

Cement is one of the most important building material of the present time. It is a dirty greyish heavy powder containing calcium aluminates and silicates. The important raw materials needed for the manufacture of cement are limestone, clay and gypsum. The main step in the manufacture of cement is the heating of raw meal or slurry in the rotary kiln at a very high temperature 1400–1600°C. Finally 2% or 3% gypsum is added.

When cement is mixed with water and left as such for sometime, it becomes a hard mass. This is known as setting of cement. It is believed that various aluminates and silicates present in the cement form hydrates with water which separate in the form of gel. The gel formed start losing water partly by evaporation and partly by forming hydrates with unhydrated constituents. This results in the formation of a hard mass.

20. Portland cement does not contain
    (1) $CaSiO_4$ (2) $CaSiO_3$
    (3) $Ca_3.Al_2O_6$ (4) $Ca_3(PO_4)_2$

21. Setting of cement is
    (1) Exothermic reaction (2) Endothermic reaction
    (3) Hydration process (4) None of these

22. The percentage of lime in Portland cement is approximately
(1) 20–25 % (2) 30–45%
(3) 60–65% (4) 40–50%

23. Concrete is a mixture of
(1) Cement, sand, gravel and water
(2) Cement, limestone and water
(3) Cement, slaked lime and water
(4) Cement, sand and water

24. Gypsum is added to Portland cement
(1) To fasten the process of setting
(2) To slow down the process of setting
(3) To improve the colour of the cement
(4) All of the above are incorrect

Paragraph 6

Alkaline earth metal nitrate (A) on heating decomposes, leaving a solid residue (B) which goes into solution with dilute HCl. The solution of (B) gives a white precipitate (C) with ammonium carbonate solution. The precipitate (C) is dissolved in dilute HCl and the solution is treated with potassium chromate to get yellow precipitate (D). The solution (B) with dilute H_2SO_4 also gives a white precipitate (E) insoluble in diute HCl and nitric acid. The precipitate (E) is a part of a white pigment lithopone.

25. The compound (E) is
(1) $BaSO_4$ (2) $MgSO_4$
(3) $CaSO_4$ (4) Na_2SO_4

26. The yellow precipitate (D) is
(1) $PbCrO_4$ (2) $BaCrO_4$
(3) $CaCrO_4$ (4) none of these

27. The metal nitrate (A) is
(1) $Ca(NO_3)_2$ (2) $Pb(NO_3)_2$
(3) $Ba(NO_3)_2$ (4) KNO_3

28. The solid residue (B) is
(1) CaO (2) PbO
(3) ZnO (4) BaO

29. The nitrate (A) can be confirmed by flame test. The colour imparted by the salt to the Bunsen flame is
(1) Yellow (2) Green
(3) Blue (4) Red

Paragraph 7

Both alkali metals and alkaline earth metals are s-block elements. They resemble each other in many respects but still there are certain dissimilarities in their properties due to different number of electrons in the valence shell, different atomic radii, ionisation enthalpy, electronegativity, etc.

Like lithium, Be also differs from rest of the alkaline earth metals on account of its small atomic size and high electronetativity. Be^{2+} ion is very small and exerts a high polarising effect on any anion associated with it.

30. The correct sequence of increasing covalent character is
(1) $BeCl_2 < NaCl < LiCl$ (2) $NaCl < LiCl < BeCl_2$
(3) $BeCl_2 < LiCl < NaCl$ (4) $LiCl < NaCl < BeCl_2$

31. Which is least thermally stable?
(1) Li_2CO_3 (2) $MgCO_3$
(3) $BaCO_3$ (4) $BeCO_3$

32. Which of the following statements are true for group 2 elements?
(1) Lattice enthalpy of oxides, carbonates, fluorides decreases from Be to Ba.
(2) All form nitrides in air.
(3) The solubility of the hydroxides increases from Be to Ba.
(4) All are correct.

33. The alkaline earth metal which does not directly combine with hydrogen is
(1) Be (2) Ca
(3) Sr (4) Ba

34. The solubility in water of sulphates down the group (↓) is Be > Mg > Ca > Sr > Ba. This is due to
(1) Increase in melting point
(2) Increase in molecular mass
(3) Decrease in lattice enthalpy
(4) High heat of solvation for smaller ions

35. Which of the bicarbonate does not exist in solid state?
(1) $NaHCO_3$ (2) $KHCO_3$
(3) $Ca(HCO_3)_2$ (4) $RbHCO_3$

36. The element which does not directly combine with carbon on strong heating:
(1) Li (2) Be
(3) K (4) Ca

Paragraph 8

Limestone is a naturally occurring form of calcium carbonate. It is used as building material and also for manufacture of other building materials such as Portland cement. It is used for the production of quicklime and slaked lime which have wide applications in chemical, metallurgical and construction industry. The pure $CaCO_3$, called precipitated calcium carbonate, is used extensively as filler, providing bulk to materials such as paint, plastics, printing inks and rubber. It is also used in toothpastes, cosmetics and antacids. Quicklime and slaked lime are the cheapest and the most widely used bases for neutralising unwanted acids. Lime is used to neutralise acidic soils. An important application of quicklime is in air pollution control for the removal of SO_2 in electric power plants. Slaked lime is used in the manufacture of other alkalis and bleaching powder, in sugar refining, in tanning hides and in water softening.

37. The substance not likely to contain $CaCO_3$ is
(1) Dolomite (2) A marble statue
(3) Sea shells (4) Calcined gypsum

38. Slaked lime reacts with chlorine to give
(1) $CaCl_2$ (2) CaO
(3) $CaOCl_2$ (4) $CaCO_3$

39. Quicklime is
(1) CaO (2) $CaCO_3$
(3) $Ca(OH)_2$ (4) $CaSO_4$

40. The drying agent which absorbs CO_2 and reacts violently with water is

(1) Sodium carbonate (2) Quicklime
(3) Conc H_2SO_4 (4) Alcohol

41. Chemical compound (A) is used to remove temporary hardness from water. It reacts with Na_2CO_3 to generate caustic soda. When CO_2 is passed through (A) it turns cloudy. What is (A)?

(1) $CaCO_3$ (2) $Ca(HCO_3)_2$
(3) $Ca(OH)_2$ (4) $CaCl_2$

42. Quicklime is used in electric power plants with carbon to check pollution. What product of calcium is formed?

(1) $CaSO_3$ (2) $CaSO_4$
(3) CaS (4) $CaSO_4 \cdot 10H_2O$

Matrix Match Type

This section contains questions each with two columns–I and II. Match the items given in column I with that in column II.

1.

	Column I		Column II
a.	Dolomite	i.	Radium
b.	Beryl	ii.	$Ca_3(PO_4)_3F$
c.	Fluorapatite	iii.	$3BeO \cdot Al_2O_3 \cdot 6SiO_2$
d.	Chrysoberyl	iv.	$MgCO_3 \cdot CaCO_3$
e.	Witherite	v.	$BeO \cdot Al_2O_3$
f.	Belgian Congo	vi.	$BaCO_3$

2.

	Column I		Column II
a.	Norwegian saltpetre	i.	CaO
b.	Superphosphate of lime	ii.	$Ca(OH)_2$
c.	Kiesserite	iii.	$Ca(Na_3)_2$
d.	Fluorspar	iv.	$MgSO_4 \cdot 7H_2O$
e.	Milk of lime	v.	CaF_2
f.	Lime	vi.	$Ca(H_2PO_4)_2 \cdot 2H_2O + 2CaSO_4 \cdot 2H_2O$

3. Match the itmes given in column I with that in Column II and III.

Column I		Column II		Column III	
Characteristics (I)		Alkaline earth metals		Characteristics (II)	
a.	Carnalite	i.	Ca	p.	Lowest thermal stabilities of their carbonates
b.	Gypsum	ii.	Ba	q.	Its carbide react with water to give acetylene (C_2H_2) gas
c.	Highest solubilities of their hydroxides and fluorides in water	iii.	Mg	r.	Its carbide react with water to give propyne ($CH_3-C \equiv CH$) gas
d.	Its carbide reacts with water to give CH_4 gas	iv.	Be	s.	Lowest ionisation enthalpy
				t.	It exhibits similarity in their properties with Al.

For Q.4 to Q.7

Answer the questions given below by appropriately matching the information given in three column of the following table.

Column I		Column II		Column III	
E.C. of 1st group elements		Characteristics (I)		Characteristics (II)	
a.	$4s^2$	i.	Strongest reducing agent	p.	Brick red in flame colouration
b.	$3s^2$	ii.	On heating with excess of air forms peroxides	q.	Don't show flame colour
c.	$2s^2$	iii.	Its chloride in solid state exists in polymeric chain structure	r.	On heating with excess of air form oxides
d.	$6s^2$	iv.	Ingredient used in toothpaste	s.	Lowest solubility of their sulphates and carbonates in water

4. For calcium, correct combination is

(1) d–i, ii–s (2) b–iv–q
(3) a–ii–p (4) b–iv–q, r

5. For beryllium, correct combination is

(1) c–iii–q,r (2) c–iii–q
(3) c–iv–q (4) c–iv–q, r

6. For barium, correct combination is

(1) d–i–s (2) d–i, ii–s
(3) c–ii–p (4) d–ii–s

7. For magnesium, correct combination is

(1) a–ii–p (2) d–i, ii–s
(3) b–iv–q (4) b–iv–q, r

8. Match the items given in Column I with that in Column II.

	Column I (Chemical Properties)		Column II (Metals)
a.	Metal + NH_3 (liquid) $\rightarrow$ Blue solution	p.	Sr
b.	MCl_2 + conc. $H_2SO_4 \rightarrow$ White ppt.	q.	Mg
c.	Metal sulphate $\xrightarrow{\Delta}$ Metal oxide + SO_2 + O_2	r.	Na
d.	Metal cation + $CrO_4^{2-} \rightarrow$ Yellow ppt.	s.	Ba

9. Match the items given in Column I with that in Column II.

	Column I (Chemical eq. related to compounds)		Column II (Compounds in excess amounts)
a.	$Ag^{\oplus}$ salt $\rightarrow$ Soluble complex	p.	$Na_2S_2O_3$
b.	$Fe^{3+} \rightarrow Fe(OH)_3$	q.	Na_2SO_3
c.	$Fe^{+3} \rightarrow Fe^{+2}$	r.	NaOH
d.	$S \rightarrow S_2O_3^{2+} + S^{2-}$	s.	KOH

Numerical Value Type

1. How many alkaline earth metals are known?
2. How many water molecules are associated with Epsom salt?
3. Calcium carbide reacts with nitrogen and forms an important fertiliser, calcium cyanamide. How much calcium cyanamide is formed when 6.4 g of calcium carbide is completely converted into cyanamide?
4. Magnalium is an alloy of aluminium and magnesium. What is the percentage of magnesium in this alloy?
5. Magnesium oxide when mixed with a saturated solution of $MgCl_2$, sets to a hard mass known as 'Sorel cement' is formed. The composition of Sorel cement is $MgCl_2{\cdot}nMgO{\cdot}xH_2O$. What is the value of n?
6. How many water molecules are present as water of crystallisation in gypsum?

Archives

JEE MAIN

Single Correct Answer Type

1. The solubilities of carbonates of magnesium group decreases down due to decrease in
   (1) interionic attractions
   (2) entropy of solution formation
   (3) lattice energy
   (4) hydration energy of cation **(AIEEE 2009)**
2. Which of the following process is used in the extractive metallurgy of magnesium?
   (1) Fused salt electrolysis
   (2) Self-reduction
   (3) Aqueous solution electrolysis
   (4) Thermite reduction **(AIEEE 2009)**
3. Molecular formula of Glauber's salt is
   (1) $MgSO_4{\cdot}7H_2O$ (2) $CuSO_4{\cdot}5H_2O$
   (3) $FeSO_4{\cdot}7H_2O$ (4) $Na_2SO_4{\cdot}10H_2O$ **(AIEEE 2010)**
4. In curing cement plaster, water is sprinkled from time to time. This helps in
   (1) hydrating sand and gravel mixed with cement
   (2) converting sand into silicate
   (3) developing interlocking needle like crystals of hydrated silicate
   (4) keeping it cold **(AIEEE 2011)**
5. A metal M readily forms sulphate MSO_4 which is water insoluble. It forms oxide MO which becomes inert on heating. It forms insoluble hydroxide which is soluble in NaOH. The metal M is
   (1) Mg (2) Ba
   (3) Ca (4) Be **(AIEEE 2011)**
6. Which of the following on thermal decomposition yields a basic as well as an acidic oxide?
   (1) $KClO_3$ (2) $CaCO_3$
   (3) NH_4NO_3 (4) $NaNO_3$ **(AIEEE 2012)**
7. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy?
   (1) $CaSO_4$ (2) $BeSO_4$
   (3) $BaSO_4$ (4) $SrSO_4$ **(JEE Main 2015)**
8. Both lithium and magnesium display several similar properties due to the diagonal relationship; however, the one which is incorrect is:
   (1) both form basic carbonates
   (2) both form soluble bicarbonates
   (3) both form nitrides
   (4) nitrates of both Li and Mg yield NO_2 and O_2 on heating **(JEE Main 2017)**

Answers Key

EXERCISES

Single Correct Answer Type

1. (3)	2. (3)	3. (3)	4. (2)	5. (3)
6. (4)	7. (1)	8. (3)	9. (4)	10. (1)
11. (2)	12. (2)	13. (4)	14. (1)	15. (2)
16. (2)	17. (3)	18. (2)	19. (1)	20. (1)
21. (2)	22. (3)	23. (1)	24. (1)	25. (4)
26. (3)	27. (3)	28. (1)	29. (4)	30. (3)
31. (3)	32. (1)	33. (4)	34. (3)	35. (2)
36. (2)	37. (3)	38. (2)	39. (4)	40. (3)
41. (3)	42. (2)	43. (3)	44. (4)	45. (1)
46. (4)	47. (1)	48. (3)	49. (2)	50. (3)
51. (4)	52. (3)	53. (4)	54. (4)	55. (4)
56. (2)	57. (2)	58. (4)	59. (3)	60. (2)
61. (2)	62. (2)	63. (1)	64. (1)	65. (1)
66. (2)	67. (2)	68. (2)	69. (4)	70. (2)
71. (1)	72. (3)	73. (2)	74. (4)	75. (3)
76. (2)	77. (2)	78. (1)	79. (4)	80. (3)
81. (2)	82. (3)	83. (3)	84. (4)	85. (2)
86. (2)	87. (1)	88. (2)	89. (1)	90. (1)
91. (2)	92. (1)	93. (1)		

Multiple Correct Answers Type

1. (3, 4)	2. (2, 3, 4)	3. (2, 3, 4)
4. (1, 2, 3)	5. (2, 3)	6. (1, 4)
7. (3, 4)	8. (1, 2)	9. (2, 3, 4)
10. (2, 3, 4)	11. (2, 3, 4)	12. (1, 2, 3, 4)
13. (2, 3)	14. (2, 3)	15. (3, 4)
16. (1, 2)	17. (3, 4)	18. (1, 2, 3)
19. (1, 2, 3, 4)	20. (3, 4)	21. (1, 3)
22. (1, 2)	23. (1, 2, 4)	24. (1, 2, 3)
25. (1, 2, 3)	26. (1, 2)	27. (1, 4)
28. (2, 3, 4)	29. (1, 2, 3, 4)	

Linked Comprehension Type

1. (2)	2. (1)	3. (3)	4. (1)	5. (1)
6. (3)	7. (2)	8. (2)	9. (2)	10. (3)
11. (2)	12. (2)	13. (1)	14. (1)	15. (4)
16. (1)	17. (1)	18. (1)	19. (1)	20. (4)
21. (1, 3)	22. (3)	23. (1)	24. (2)	25. (1)
26. (2)	27. (3)	28. (4)	29. (2)	30. (2)
31. (2)	32. (4)	33. (1)	34. (4)	35. (3)
36. (3)	37. (4)	38. (3)	39. (1)	40. (2)
41. (3)	42. (1)			

Matrix Match Type

Q.No.	a	b	c	d	e	f
1.	iv	iii	ii	v	vi	i
2.	iii	vi	iv	v	ii	i
3.	iii–r	i–q	ii–s,q	iv–p,t		

4. (3) 5. (1) 6. (2) 7. (4)

8. (a → p, r, s; b → p, s; c → p, q, s; d → p, s)

9. (a → p, q; b → r, s; c → p, q; d → r, s)

Numerical Value Type

1. (6)	2. (7)	3. (8)	4. (5)	5. (5)
6. (2)				

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Single Correct Answer Type

1. (4)	2. (1)	3. (1)	4. (3)	5. (4)
6. (2)	7. (2)	8. (1)		

6 p-Block Group 13 Elements The Boron Family

OVERVIEW

Group 13: The Boron Family

1. Group 13 of the periodic table constitutes boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl). This group of elements belongs to *p*-block and marks the beginning of *p*-block elements.
2. General electronic configuration: $ns^2\ np^1$.
3. Aluminium is the most abundant metal and the third most abundant element after oxygen and silicon by mass in the earth's crust.
4. Boron is fairly rare but occurs as concentrated deposits of borax.
5. Gallium is twice as abundant as boron but indium and thallium are much less common.
6. Atomic radii of group 13 elements are less than the corresponding group 2 elements.
   Atomic radii: B < Ga < Al < In < Tl. This irregular variation in radii, down the group (↓), is due to inclusion of fully filled lesser shielding 3*d* orbital in Ga, 4*d* orbital in In and 4*f* and 5*d* orbitals in Tl between the valence shell electrons and noble gas core. Consequently, the valence shell electrons experience greater force of attraction and thereby causing an irregular variation in radii.
7. First ionisation enthalpy of group 13 elements is less than the first ionisation enthalpy of corresponding group 2 elements, as *p*-electrons are less penetrating and hence less tightly held than *s*-electrons.
   The ionisation enthalpy values vary irregularly as follows: B > Ga > Al > Tl > In. This is due to the presence of fully filled lesser shielding *d* and/or *f*-orbitals in between the valence shell electrons and noble gas core in Ga, In and Tl.
   The successive ionisation enthalpies vary in the order: $IE_1 > IE_2 > IE_3$.
8. The elements of group 13 are less electropositive or metallic as compared to corresponding group 1 and 2 elements.
9. **Electropositive character:** Al > B > Ga > In > Tl. Boron having the highest sum total of first three ionisation enthalpies is least metallic or behaves as a non-metal. Aluminium is the most metallic. The remaining three are weakly metallic.
10. Group 13 elements have higher densities as compared to corresponding group 2 elements due to their smaller atomic and ionic radii. Down the group (↓), density varies in the order: B < Al < Ga < In < Tl.
11. **Melting point:** B > Al > Tl > In > Ga. Abnormally high melting point of boron is due to the fact that it exists as B_{12} (icosahedron structure) in both solid and liquid state. Boron exists as Gallium consists of unusual structure. It consists of only Ga_2 molecules. Gallium's melting point is 30°C and it exists as a liquid up to 2000°C and hence is used in high temperature thermometry. Al, In and Tl have closed packed metal structure.
12. **Boiling point:** B > Al > Ga > In > Tl.
13. The reluctance of ns^2 electrons to unpair and participate in the chemical bond formation is known as *inert pair* effect. This gives rise to the concept of variable valency.
14. B and Al exhibit an oxidation state of +3 (i.e. group oxidation state). Ga, In and Tl, besides +3 oxidation state also show an oxidation state +1 due to the inert pair effect.
15. Stability of higher oxidation state, +3 decreases in the order : B > Al > Ga > In > Tl. Stability of lower oxidation state, +1 increases in the order : Ga < In < Tl.
16. Tl(III) compounds behave as strong oxidising agents, whereas Ga(I) compounds behave as strong reducing agents.
    Gallium is apparently divalent in few compounds such as $GaCl_2$, but actually it is $\overset{+1}{Ga}[\overset{+3}{Ga}Cl_4]$.
17. Bonding in compounds of group 13 is mainly covalent, due to the following:
    a. Small size and high charge of ions, resulting in high polarising ability (charge/radius ratio).
    b. Very high sum total of the first three ionisation enthalpies
    c. High electronegativity values.
    Boron always forms covalent compounds. In the anhydrous state, $AlCl_3$, $GaCl_3$ are covalent, whereas in the solution state Al, Ga, In and Tl form metal ions due to the high hydration enthalpy. Thallium compounds are ionic in nature.
18. Pure boron is less reactive than impure finely powdered boron, which burns in air forming oxide. Al reacts with air to form oxide layer on its surface, which prevents it from

further attack. In industry, the oxide film on Al is purposely increased by *anodising*. Anodised cooking vessels are used as non-stick cookwares.

Ga and In are not affected by air. Tl forms an oxide layer on its surface. B and Al combine with nitrogen and carbon on heating to form nitrides and carbides respectively.

Boron carbide (B_4C) is the hardest known artificial substance and is called *morbide*.

19. **Reactivity towards water:** Boron is unaffected by water or steam. Al decomposes cold water, if the oxide layer is not present on its surface. Ga and In are not attacked by water, unless O_2 is present. Tl is attacked by moist air.

20. Boron is not affected by non-oxidising agents, while other elements dissolve forming trivalent salts. The oxidising acids react with all the elements. However, Al and Ga become passive with conc HNO_3 due to the formation of oxide layer.

21. B, Al and Ga react with alkalis, evolving H_2, but In and Tl remain unaffected.

22. With halogens, all these elements form corresponding halides.

23. Boron combines with metals on heating to form borides. The rest of the elements do not combine with metals.

24. Group 13 elements have greater complex forming tendency as compared to *s*-block elements due to the following:

a. Small size

b. High charge

c. Availability of vacant *d*-orbitals

25. All group 13 elements form oxides of the type M_2O_3. Al_2O_3 exist in α and γ form. α-alumina is called *corundum*.

It is hard, refractory material and is used as an *abrasive*.

γ-alumina is also known as *activated alumina* and is used in chromography (due to its large surface area). Thallium also forms Tl_2O which is more stable and behaves as an alkali metal oxide. Ga is used in high temperature thermometer (due to lowest melting point).

26. Down the group ($\downarrow$), there is a gradual change from acidic to amphoteric and then to basic character of the oxides.

$$\underset{\text{Acidic}}{B_2O_3}\quad \underbrace{Al_2O_3\quad Ga_2O_3}_{\text{Amphoteric}}\quad \underbrace{In_2O_3\quad Tl_2O_3}_{\text{Basic}}$$

27. Group 13 elements form hydroxides of the type, $M(OH)_3$. Down the group ($\downarrow$), there is a gradual change from acidic to amphoteric and then to basic character.

$$\underset{\text{Acidic}}{B(OH)_3}\quad \underbrace{Al(OH)_3\quad Ga(OH)_3}_{\text{Amphoteric}}\quad \underbrace{In(OH)_3\quad Tl(OH)_3}_{\text{Basic}}$$

28. Group 13 elements do not combine with hydrogen directly, however, a number of hydrides are known. Boron forms a number of stable covalent hydrides, namely closoboranes, $B_nH_{(n+4)}$ and nidoboranes, $B_nH_{(n+6)}$. Boranes are electron-deficient compounds. Aluminium forms a polymeric hydride, Alane $(AlH_3)_n$. Gallium forms dimeric hydride, digallane (Ga_2H_6). Indium forms a polymeric hydride. Thallium does not form any hydride.

B, Al and Ga form complex anionic hydrides such as $NaBH_4$, $LiAlH_4$ and $LiGaH_4$.

29. Group 13 elements form trihalides, MX_3. Boron trihalides are covalent. Being electron-deficient compounds, they act as Lewis acids. The trifluorides of Al, Ga, In and Tl are ionic while the chlorides, bromides and iodides are largely covalent when anhydrous.

However, the covalent nature decreases on moving from Ga to Tl. Trihalides fume in air and undergo hydrolysis. They also act as Lewis acids. Tendency to undergo hydrolysis decreases down the group ($\downarrow$) with decrease in charge/radius ratio of the cation.

30. Boron halides complete their octet by back-donation, whereas other members form dimers. The dimer form exists in vapour and non-polar solvents. In aqueous solution, the dimer form disappears as it get ionised to form $[M(H_2O)_6]^{3+}$ and 3 $X^{\ominus}$ ions due to high hydration enthalpy.

31. Borax is also known as *Tincal* or *Suhaga*. Tincal contains 45% borax. Borax exists in three forms:

a. Prismatic borax—$Na_2B_4O_7 \cdot 10H_2O$

b. Octahedral borax—$Na_2B_4O_7 \cdot 5H_2O$ (also known as **Jeweller's borax**)

c. Anhydrous borax—$Na_2B_4O_7$ (also known as *borax glass*)

32. Borax on heating swells due to elimination of water and then melts, which solidifies to transparent glassy bead.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \xrightleftharpoons{740^\circ} \underbrace{2NaBO_2 + B_2O_3}_{\text{Glassy bead}}$$

Glassy bead when heated with coloured salt in oxidising and reducing flame, gives characteristic colours. This is known as borax bead test.

33. Boron exists in two forms: amorphous and crystalline. Amorphous boron is chemically active, whereas crystalline boron is inert. Boron is used as a deoxidiser in the casting of copper and for making boron steel which are used as control rods in nuclear reactors.

34. Diborane (B_2H_6) is the simplest hydride of boron. With ammonia, at $-120°C$ it forms $[B_2H_2(NH_3)_2]^{\oplus}[BH_4]^{\ominus}$. When this product is heated at 200°C, $B_3N_3H_6$; *borazol or inorganic benzene* is formed. On strong heating, borazon $(BN)_x$ is formed. Borazon is harder than diamond. It is used as an abrasive.

35. On heating borazine, a product similar to naphthalene, known as *inorganic naphthalene* is formed.

36. The relative Lewis acid strength of boron trihalides is $BF_3 < BCl_3 < BBr_3 < BI_3$. This is due to the back-donation of election pair from filled np_z orbital on halogen to vacant $2p_z$ orbital on B-atom.

37. Aluminium due to its lightness, good conductivity and resistance to corrosion is used for making alloys.

Alloy	Composition
Magnalium	95% Al + 5% Mg
Duralumin	95% Al + 4% Cu + 0.5% Mg + 0.5% Mn
Aluminium bronze	90% Cu + 9.5% Al + 0.5% Sn
Nickeloy	95% Al + 4% Cu + 1% Ni
γ-alloy	93% Al + 4% Cu + 2% Ni + 1% Mg
Alnico	77% steel + 20% Al + 2% Al + 2% Ni + 1% Co

Thin foils of Al are used for wrapping soaps, confectionary etc. Al wire is used in transmission lines and coils for dynamos and motors. It is also used as silver paint and in thermite process.

38. Anhydrous $AlCl_3$ is prepared by passing dry HCl or Cl_2 gas over heated Al turnings in absence of air. Anhydrous $AlCl_3$ is covalent, whereas hydrated $AlCl_3 \cdot 6H_2O$ is ionic.

39. Alum is used to describe any double salt having the composition $\overset{1+}{M_2}SO_4 \cdot \overset{3+}{M_2}(SO_4)_3 \cdot 24H_2O$. The most commonly known alum is potash alum,
$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$. It is used as an antiseptic, as a mordant in dyeing, in leather tanning and water softening.

40. *Ultramarine* is an artificial Lapis Lazuli, a rare mineral ($Na_3Al_3Si_3S_2O_{12}$), which has fine blue colour and is used in making blue paint.

41. Pseudoalums are double sulphates of divalent ions and trivalent ions with 24 water molecules of crystallisation, e.g., $\overset{2+}{M}SO_4 \cdot \overset{3+}{M_2}(SO_4)_3 \cdot 24H_2O$. These are not isomorphous with alums.

42. Aluminium acetate, commonly known as *red liquor*, is used as a mordant in dyeing and calico painting.

43. The most toxic element of group 13 is thallium.

6.1 GROUP 13: THE BORON FAMILY

The elements in which the last electron enters the outermost *p*-orbital are known as *p*-block elements. As there are three degenerate (same energy) *p*-orbitals, in the *p*-subshell, each of which can accommodate two electrons, therefore the maximum number of electrons that can be accommodated in a set of *p*-orbitals is six. Hence, there are six groups of *p*-block elements in the periodic table, i.e. 13, 14, 15, 16, 17 and 18. Boron, carbon, nitrogen, oxygen, fluorine and helium heads the groups.

6.2 GENERAL CHARACTERISTICS OF THE *p*-BLOCK ELEMENTS

6.2.1 ELECTRONIC CONFIGURATION AND OXIDATION STATES

The valence shell electronic configuration of *p*-block elements is ns^2np^{1-6} (except helium). The inner core of their electronic configuration may, however, differ. The difference in the inner core of elements greatly influences their physical properties (such as atomic and ionic radii, ionisation enthalpy, electronegativity, etc.) as well as chemical properties. As a result, a lot of variation in properties of elements in a group of a *p*-block is observed.

The maximum (or highest) oxidation state shown by a *p*-block element is equal to the total number of valence electrons, i.e. the sum of *s*- and *p*-electrons, or the group number minus 10. The maximum oxidation state is also known as *group oxidation state*. In addition to the group oxidation state, *p*-block elements may show other oxidation states. As the number of *s*- and *p*-electrons in the valence shell increases, the number of such possible oxidation states increases across the period (→). These oxidation states usually but not necessarily differ from the group oxidation state by the unit of two. The important oxidation states shown by *p*-block elements are given in Table 6.1.

Table 6.1 General electronic configuration and oxidation states of *p*-block elements

Group	13	14	15	16	17	18
General electronic configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6 ($1s^2$ for He)
First member of the group	B	C	N	O	F	He
Group oxidation state	+3	+4	+5	+6	+7	+8
Other oxidation states	+1	+2, –4	+3, –3	+4, +2, –2	+5, +3, +1, –1	+6, +4, +2

In boron, carbon and nitrogen families, the group oxidation state is the most stable state for the lighter elements in the group. However, a lower oxidation state, two unit less than the group oxidation state, becomes progressively more stable for the heavier elements in each group. The occurrence of oxidation state, two unit less than the group oxidation state, is attributed to the 'inert pair effect', and this becomes more prominent, down the group (↓). The relative stabilities of these two oxidation states, i.e. the group oxidation state and the oxidation state, two unit less than the group oxidation state, vary from group to group and will be described at appropriate places.

6.2.2 GENERAL CHEMICAL BEHAVIOUR

It is interesting to note that among the four blocks (i.e. *s*-, *p*-, *d*- and *f*-) of elements in the periodic table, the non-metals and metalloids exist only in the *p*-block of the periodic table. The common metalloids among *p*-block elements are silicon, germanium, arsenic, antimony and tellurium, while all the remaining elements are non-metals. In general, down the group (↓), non-metallic character decreases. In fact, the heaviest element in each *p*-block group is most metallic in nature. This change from non-metallic to metallic character brings diversity in the chemistry of these elements depending on the group to which they belong. In general, the following is a list of characteristics:

1. Non-metals have higher ionisation enthalpies and higher electronegativities as compared to metals. Therefore, in contrast to metals, which readily form cations, non-metals readily form anions.
2. The compounds formed between highly reactive metals and highly non-reactive non-metals are generally ionic because of large differences in their electronegativities.
3. The compounds formed between non-metals themselves are largely covalent in character because of small differences in their electronegativities.

The change from non-metallic to metallic character can best be illustrated by the nature of oxides they form. The oxides of non-metals are either acidic or neutral, whereas the oxides of metals are always basic in nature. However, oxides of metalloids are amphoteric. In general, the more electropositive the metal, the more basic is its oxide and the more electronegative the non-metal, more acidic is its oxide.

Therefore, among *p*-block elements across a period (→), the acidic character of the oxides increases or basic character decreases.

Down the group (↓), the basic character of the oxide increases or the acidic character decreases.

6.2.3 DIFFERENCE BETWEEN FIRST MEMBER AND THE REMAINING MEMBERS OF THE SAME GROUP

The first member of each group of *p*-block elements (particularly 13–17) differs from its succeeding members (also known as congeners) of their respective group in two major respects:

1. **Size and all other properties which depend upon size:** First element of each group of *p*-block elements differs from the rest of the members of their respective groups in much the same way as the first element of each group of *s*-block elements, i.e. lithium or beryllium differs from the rest of the elements of their respective groups. This is due to the following:
   - **a.** Small size
   - **b.** High electronegativity
   - **c.** High ionisation enthalpy
2. **Absence of *d*-orbitals in their valence shell:** Some differences arise due to the absence of *d*-orbitals in the elements of second period and the presence of *d*-orbitals in the heavier elements, few of them are as follows:

a. **Maximum covalency of four:** The first member of each group, i.e. the elements of the second period has four orbitals (one 2*s* and three 2*p*-orbitals) in the valence shell and hence can accommodate at the maximum four pairs or eight electrons. In other words, these elements show a maximum covalency of four. In contrast, the elements of third (and higher) periods of *p*-block elements have vacant 3*d*-orbitals lying between 3*p* and 4*s* level of energy. Using these orbitals, these elements can accommodate more electrons and hence can expand their maximum covalence beyond four. For example,

i. While boron forms only $[BF_4]^{\ominus}$ ion, Al can form $[AlF_6]^{3-}$ ion.

ii. Carbon can form tetravalent compounds only, e.g. CCl_4 etc. whereas Si and Ge can form $[SiCl_6]^{2-}$, $[GeCl_6]^{2-}$ etc.

b. **Chemical reactivity:** Due to the presence of *d*-orbitals, the elements of the third (and higher) periods are more reactive as compared to the second period elements. For example, CCl_4 does not undergo hydrolysis whereas $SiCl_4$ readily gets hydrolysed.

c. **Tendency to form multiple bonds:** The combined effect of size and availability of *d*-orbitals greatly affect the ability of these elements to form π-bonds. Thus, the first member of each group differs from the heavier elements in its tendency to form $p\pi$–$p\pi$ multiple bonds to itself (e.g. C=C, C≡C, N≡N) or with the other elements of the second period (e.g. C=O, C=N, C≡N, N=O). This type of $p\pi$–$p\pi$ bonding is, however, not strong in case of heavier *p*-block elements. The heavier elements also form π–bonds but this involves *d*-orbitals i.e. $d\pi$–$p\pi$ or $d\pi$–$d\pi$. Because the *d*-orbitals are of higher energy than the *p*-orbitals, they contribute less to the overall stability of molecules than does $p\pi$-$p\pi$ bonding of the second period elements. However, the coordination number in species of heavier elements may be higher than the first element in the same oxidation state. For example, in +5 oxidation state, both N and P form oxoanions: $NO_3^{\ominus}$ (three coordination with π-bond involving one nitrogen *p*-orbital) and PO_4^{3-} (four-coordination involving *s*, *p* and *d*-orbitals contributing to the π-bond).

6.3 GROUP 13 ELEMENTS—THE BORON FAMILY

Group 13 consists of boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl). Boron is a typical non-metal; aluminium is a metal but shows many chemical similarities to boron and gallium. Indium and thallium are almost exclusively metallic in character.

6.3.1 Abundance and Occurrence

Boron occurs in two isotopic forms: ${}^{10}_{5}B$ (19%) and ${}^{11}_{5}B$ (81%). The relative abundance of boron in the earth's crust is less than 0.0001% by mass. The important minerals of boron are as follows:

- Borax: $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$ or $Na_2B_4O_7\cdot 10H_2O$
- Orthoboric acid: H_3BO_3
- Kernite: $Na_2[B_4O_5(OH)_4]$ or $Na_2B_4O_7\cdot 2H_2O$
- Colemanite: $Ca_2[B_3O_4(OH)_3]_2\cdot 2H_2O$ or $Ca_2B_6O_{11}\cdot 5H_2O$

Boron in the form of borates is mainly found in the Turkey and California (USA). In India, borax occurs in the Puga Valley (Ladakh) and the Sambhar Lake (Rajasthan).

6.3.2 Isolation of Boron

Four important methods for the preparation of elemental boron are as follows:

1. Reduction of boron oxide by an electropositive metal.

$$B_2O_{3(s)} + 3Mg_{(s)} \longrightarrow 2B_{(s)} + 3MgO_{(s)}$$

$$KBF_{4(\text{Fused})} \xrightarrow{\text{Electrolysis}} K^{\oplus} + BF_4^{\ominus}$$

At cathode: $K^{\oplus} + e^{\ominus} \longrightarrow K_{(\text{Reduction})}$

At anode: $BF_4^{\ominus} \longrightarrow B + 2F_2 + e^{\ominus}{}_{(\text{Oxidation})}$

2. Electrolytic reduction of fused borates or tetrafluoroborates (KBF_4) in molten KCl/KF at 1073 K.

3. The reduction of a volatile boron compound by dihydrogen at high temperature on a heated tantalum filament.

$$2BCl_{3(g)} + 3H_{2(g)} \xrightarrow{1270\text{ K}} 2\,B_{(s)} + 6\,HCl_{(g)}$$

Boron of high purity (~ 99.9%) can be prepared by this method.

4. By thermal decomposition of boranes and boron halides at temperatures ~1173 K.

Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%).

Important minerals of aluminium are as follows:

1. Bauxite (hydrated aluminium oxide): $Al_2O_3\cdot 2H_2O$
2. Cryolite (sodium aluminium fluoride): Na_3AlF_6
3. Corundum (anhydrous alumina): Al_2O_3
4. Beryl: $3BeO\cdot Al_2O_3\cdot 6SiO_2$ or $Be_3Al_2Si_6O_{18}$
5. Mica (muscovite): $K_2O\cdot 3Al_2O_3\cdot 6SiO_2\cdot 2H_2O$ or $KAl_2(Si_3AlO_{10})(OH)_2$

In India, aluminium in the form of mica is found in Katni, Rewa (Madhya Pradesh), Belgaum (Karnataka), Orissa and Jammu.

Gallium, Indium and thallium are less abundant than aluminium. Highest concentration of Ga (0.1–1%) is found in the rare mineral *germanite* which is a complex sulphide of Zn, Cu, Ge and As.

Indium is found in traces in the sulphide ores of zinc, while thallium is found in the sulphide ores of lead. Abundance of group 13 elements in the earth's crust is given in Table 6.2

Thallium is also known as '*duckbill platypus*' as it shows similarity with many other elements.

6.4 GENERAL TRENDS IN ATOMIC AND PHYSICAL PROPERTIES

Some important atomic and physical properties of group 13 elements as mentioned in Table 6.2 are discussed below.

Property	Boron	Aluminium	Gallium	Indium	Thallium
Symbol	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
Atomic mass (g mol^{-1})	10.81	26.98	69.72	114.82	204.38
Electronic configuration	[He] $2s^2\,2p^1$	[Ne] $3s^2\,3p^1$	[Ar] $3d^{10}\,4s^2\,4p^1$	[Kr] $4d^{10}\,5s^2\,5p^1$	[Xe] $4f^{14}\,5d^{10}\,6s^2\,6p^1$
Atomic radii (pm)	(88)	143	135	167	170
Ionic radii, M^{3+} (pm)	(27)	53.5	62.0	80.0	88.5
Ionic radii, $M^{\oplus}$ (pm)	—	—	120	140	150
Ionisation enthalpy (kJ mol^{-1})					
IE_1	801	577	579	558	589
IE_2	2427	1816	1979	1820	1971
IE_3	2659	2744	2962	2704	2877
Electronegativity (Pauling)	2.0	1.5	1.6	1.7	1.8
Density (g cm^{-3}) at 298 K	2.35	2.70	5.90	7.31	11.85
Melting point (K)	2453	933	303	430	576
Boiling point (K)	3923	2740	2676	2353	1730
$E^{\ominus}$ (V) for $M^{3+}_{(aq)}/M_{(s)}$	(–0.87)	–1.66	–0.56	–0.34	+1.26
$E^{\ominus}$ (V) for $M^{\oplus}_{(aq)}/M_{(s)}$	—	+0.55	–0.79 (acid) –1.39 (alkali)	–0.18	–0.34

6.4.1 Electronic Configuration

The valence shell of group 13 elements are characterised by the configurations $ns^2\,np^1$. But there is an important difference in the complete electronic configuration of boron and aluminium on one hand and gallium, indium and thallium on the other. While boron and aluminium have a noble gas core beneath the valence shell, gallium and indium have fully filled d^{10}-core ($3d^{10}$, $4d^{10}$ respectively) present in between the noble gas core and valence shell, thallium has fully filled $5d^{10}$ and $4f^{14}$ core present in between the noble gas core and the valence shell. Thus the electronic configuration of group 13 elements is more complex as compared to group 1 and 2 elements. This difference in the electronic configuration seems to influence substantially the other properties and consequently the chemistry of all the elements of this group. The electronic configuration of the elements of group 13 is given in Table 6.3.

Table 6.3 Electronic configuration

Element	Electronic configuration
Boron (B) (Z = 5)	[He] $2s^2\,2p^1$
Aluminium (Al) (Z = 13)	[Ne] $2s^2\,2p^1$
Gallium (Ga) (Z = 31)	[Ar] $3d^{10}\,4s^2\,4p^1$
Indium (In) (Z = 49)	[Kr] $4d^{10}\,5s^2\,5p^1$
Thallium (Tl) (Z = 81)	[Xe] $4f^{14}\,5d^{10}\,6s^2\,6p^1$

6.4.2 Atomic and Ionic Radii

Statement: The atomic and ionic radii of group 13 elements are less than the corresponding group 2 elements.

Explanation: Along the period (→), i.e. from group 2 to group 13 in a given period, the nuclear charge increases but the electron enters the same shell, which results in the increase in the effective

nuclear charge and the valence shell electrons are pulled in more strongly towards the nucleus, which results in the decrease in atomic radii.

Statement: Down the group (↓), both atomic and ionic radii are expected to increase due to addition of new shell with each succeeding element. However, a deviation is observed on moving from Al to Ga. Atomic radii of Al (143 pm) is greater than that of Ga (135 pm).

Explanation: The reason lies in the difference in electronic configuration of Al and Ga.

Al (13): $[Ne]\ 3s^2\ 3p^1$

Ga (31): $[Ar]\ 3d^{10}\ 4s^2\ 4p^1$

Gallium has fully filled $3d^{10}$ orbital present between the valence shell electrons and noble gas core. As the *d*-orbitals are larger in size as compared to *s*- and *p*-orbitals, these intervening electrons do not shield the nucleus effectively. As a consequence, in gallium, the force of attraction between the valence shell electrons and the nucleus is larger as compared to that in aluminium or in other words, effective nuclear charge of gallium is greater than that of aluminium. Hence, atomic radii of aluminium is greater than that of gallium.

Ionic radii, however, follow a regular trend and keep on increasing from B to Tl.

6.4.3 Ionisation Enthalpy

Statement: The first ionisation enthalpy of group 13 elements is lower than that of corresponding group 2 elements.

Explanation: This can be explained on the basis of the general electronic configuration of group 2 and group 13 elements. General electronic configuration of group 2 elements is ns^2, whereas that of group 13 elements is $ns^2\ np^1$. First ionisation enthalpy for group 2 elements is the minimum energy required to remove an electron from ns^2 orbital, whereas for group 13 elements, it corresponds to the removal of electron from np^1 orbital. Firstly, since valence shell (ns^2 orbital) in group 2 elements is fully filled, electronic configuration is more stable and hence more energy is required for the removal of valence shell electron as compared to group 13 elements. Secondly, *ns*-orbital is more penetrating as compared to *np*-orbital, electron in *ns*-orbital is more attracted than the electron in *np*-orbital and hence removal of electron from *ns*-orbital requires more energy as compared to *np*-orbital. Because of the above-mentioned reasons, the first ionisation enthalpy of group 13 elements is lower than that of the corresponding group 2 elements. For example, the first ionisation enthalpy of B is less than that of Be.

Statement: Down the group (↓), the ionisation enthalpy values, as expected from general trends, do not decrease smoothly. From B to Al, the first ionisation enthalpy decreases from Al to Ga, there is a slight increase only but the first ionisation enthalpy of Tl is much higher than those of Al, Ga and In.

Explanation: The first ionisation enthalpy decreases from B to Al because of the increase in atomic size and screening effect which overcomes the effect of the increased nuclear charge. From Al to Ga, there is a slight increase. In Ga, In and Tl there is inclusion of fully filled lesser shielding *d* and/or *f*-orbitals in between the valence shell and noble gas core. (The shielding effect is in the order: $ns > np > nd > nf$.) As a result, the valence shell electrons are more tightly held by the nucleus and more energy is required for their removal. That is why from Al to Ga, there is a slight increase in the value of ionisation enthalpy.

From Ga to In, the increased shielding effect, due to the presence of additional 4*d* electrons is more than the effect of increased nuclear charge and hence the first ionisation enthalpy of In is lower than that of Ga. Thereafter, the effect of increased nuclear charge is more than the effect of shielding effect due to the presence of fully filled 4*f* and 5*d* electrons and hence the first ionisation enthalpy of Tl is higher than that of In (Table 6.2).

$$\begin{array}{lccccccccc} IE_1: & B & > & Al & \sim & Ga & < & In & > & Tl \\ & (801) & & (577) & & (579) & & (558) & & 589\ \text{kJ mol}^{-1} \end{array}$$

The successive ionisation enthalpies increase in the order: $IE_1 < IE_2 < IE_3$, as expected.

6.4.4 Electronegativity

Statement: Down the group (↓), electronegativity first decreases from B to Al and then increases marginally from Al to Tl.

Explanation: This is because of discrepancies in atomic size of the elements. From B to Al, the atomic size increases considerably hence the force of attraction between the nucleus and electrons decreases and electronegativity decreases. Thereafter, in spite of the fact that the size increases, the effective nuclear charge also increases due to the presence of fully filled lesser shielding *d*/*f*-orbital present in between the valence shell electrons and noble gas core. As a result, the force of attraction of the nucleus for the valence shell electrons increases and the electronegativity increases from Al to Tl (Table 6.2).

6.4.5 Electropositive or Metallic Character

Statement: The elements of group 13 are less electropositive or metallic as compared to the corresponding group 1 and group 2 elements.

Explanation: The electropositive character or metallic character decreases on moving from group 1 to 2 to 13 due to decrease in the tendency to lose valence shell electrons. This is due to an increase in value of ionisation enthalpies required to remove the valence shell electrons.

Statement: Down the group (↓), the electropostive character first increases from B to Al and then decreases from Al to Tl.

Explanation: Among group 13 elements, the sum of the first three ionisation enthalpies is highest for B and hence it has little tendency to lose valence shell electrons. Consequently, B is least electropositive among group 13 elements, hence it behaves as a non-metal and a poor conductor of electricity.

From B to Al, the sum of the first three ionisation enthalpies decreases substantially due to an increase in atomic size and hence electropositive character increases. Hence, Al is a metal and a good conductor of electricity.

Ga, In and Tl are less likely to lose electrons (and thus are less electropositive) due to poor shielding caused by the presence of fully filled *d* and/or *f*-orbital in between the valence shell electrons and noble gas core.

The electropostive character of the group 13 elements can also be explained on the basis of their respective electrode potentials. As the electrode potentials for the reaction, $M^{3+}_{(aq)} + 3e^{\ominus} \longrightarrow M_{(s)}$ increase from Al to Tl, hence their electropositive character decreases from Al to Tl.

The standard electrode potentials for M^{3+}/M becomes less negative from Al to Ga to In and the potential becomes positive for Tl.

Since $\Delta G = -nFE^{\ominus}$, it follows that the free energy of formation of the metal, e.g. $Al^{3+} + 3e^{\ominus} \longrightarrow Al$, is positive. Thus, it is difficult to make this reaction proceed. The reverse reaction, $Al \longrightarrow Al^{3+} + 3e^{\ominus}$ occurs spontaneously. The standard potential become less negative on descending the group so it becomes less difficult for the reaction to occur. Thus, the +3 oxidation state becomes less stable in aqueous solution, down the group (↓). Similarly, the $E^{\ominus}$ value for $M^{\oplus}/M$ show that +1 oxidation state increases in stability down the group (↓). With Tl, the +1 state is more stable than + 3 state.

Note: It should be remembered that in this type of explanation $E^{\ominus}$ and ΔG refer to the reaction with H_2.

$$Al^{3+} + \frac{3}{2} H_2 \longrightarrow Al + 3H^{\oplus}$$

6.4.6 Density

Statement: Group 13 elements have higher densities as compared to the corresponding group 2 elements.

Explanation: This is due to smaller atomic and ionic radii of group 13 elements as compared to group 2 elements, which makes density (= mass/volume) to increase.

Statement: Down the group (↓), density increases from B to Tl.

Explanation: This is due to the corresponding increase in atomic mass of the element which outweighs the effect of increased atomic size. The densities of B and Al are, however, quite lower than of other members.

6.4.7 Melting Points and Boiling Points

The melting points of group 13 elements do not show a regular trend as shown by group 1 and 2 elements. This is probably due to the unusual crystal struture of B and Ga.

Statement: Down the group (↓), the melting point decreases sharply from B to Ga and then increases from Ga to Tl.

Explanation: Boron has the highest melting point (2453 K) since its crystal structure consists of icosahedral units with B atoms at all the 12 corners and each boron atom is bonded to five equidistant neighbours. In contrast, the crystal structure of Ga is markedly different from that of B. Each Ga atom has one close neighbour at a distance of 243 pm and six more distant neighbours at a distance of 270–279 pm. This suggests that gallium consists of almost discrete diatomic molecules, Ga_2, and hence its melting point is exceptionally low (303 K) and it could exist as a liquid at room temperature in summer. In contrast, Al, In and Tl have closed packed structures. Their melting points decrease from Al to In and increase again for Tl.

However, the boiling points of these elements follow a regular trend and decrease regularly down the group (↓).

The high boiling point of gallium makes it a useful material for measuring high temperature. Another unusual property of gallium is that like Ge and Bi, liquid Ga expands when it changes into solid, i.e. ρ (solid Ga) < ρ (liquid Ga).

6.5 CHEMICAL PROPERTIES

Some of the important chemical properties of the elements of group 13 are discussed here.

6.5.1 Oxidation States and Trends in Chemical Reactivity

Oxidation states: The general electronic configuration of group 13 element is $ns^2 np^1$, i.e. they have three electrons in their valence shell, i.e. two electrons in the *ns* orbital and one electron in *np* orbital. All the elements of group 13 are expected to exhibit a characteristic oxidation state of +3, through the unpairing of two *ns*-electrons and subsequent promotion of one of them to one of vacant *np*-orbital of the same quantum shell (Fig. 6.1).

	ns	*np*
Ground state electronic configuration	⇅	↑ | |
Excited state electronic configuration	↑	↑ | ↑ |

Fig. 6.1 Ground state and excited state electronic configuration of group 13 elements

This is true for boron and aluminium, which shows an oxidation state of +3 only, but gallium, indium and thallium shows an oxidation state of +1 also, in addition to +3 oxidation state, due to inert pair effect.

Element	B	Al	Ga	In	Tl
Oxidation state	+3	(+1), +3	+1, +3	+1, +3	+1, (+3)

The elements of group 13 have general electronic configration of $ns^2 np^1$. The existence of lower oxidation state, +1, can be explained by the fact that ns^2 electrons remain paired up and do not participate in the bond formation. *The reluctance of the ns^2 electrons to unpair and to participate in the bond formation is known as inert pair effect.* If the energy required to unpair ns^2 electrons exceeds the energy evolved in forming two additional bond, then the ns^2 electrons will remain paired up and lower oxidation, i.e. +1 will be more stable as compared to the higher oxidation state, i.e. +3.

Inert pair effect arises due to the presence of fully filled lesser shielding *d* and/or *f*-orbitals in between the noble gas core and valence shell electrons. Due to poor or ineffective shielding of ns^2 electrons by the electrons present in *d* and/or *f*-orbitals (shielding effect: *ns* > *np* > *nd* > *nf*), force of attraction between the noble gas core and valence shell electrons increases and hence unpairing of ns^2 electrons requires higher energy. When the energy which is required to unpair the ns^2 electron is not compensated by the energy which is released during compound formation, unpairing of ns^2 electrons would not occur and hence lower oxidation state, i.e. +1 will be observed.

1. Down the group (↓), the stability of the higher oxidation state, i.e. +3 decreases, while that of lower oxidation state i.e. +1 increases.

Order of stability: Ga(III) > In(III) > Tl(III)

Ga(I) < In(I) < Tl(I)

Due to increase in inert pair effect down the group (↓), stability of higher oxidation state, i.e. +3 decreases, while that of lower oxidation state, i.e. +1 increases.

2. Since in the case of Ga and In, +3 oxidation state is more stable than +1 oxidation state, therefore both Ga(I) and In(I) salt undergo disproportionation (self oxidation–reduction) in aqueous solution.

$$3GaX_{(s)} \longrightarrow \overset{(0)}{2Ga_{(s)}} + \overset{(III)}{Ga^{3+}_{(aq)}} + 3X^{\ominus}_{(aq)}$$

$$3InX_{(s)} \longrightarrow \overset{(0)}{2In_{(s)}} + \overset{(III)}{In^{3+}_{(aq)}} + 3X^{\ominus}_{(aq)}$$

3. Tl(I) compounds are more stable as compared to Tl(III) compounds due to inert pair effect. For example, thallous chloride and thallous hydroxide are more stable as compared to thallic chloride and thallic hydroxide respectively.

4. Since Tl(I) is more stable than Tl(III), Tl(III) compounds behave as strong oxidsing agent. On the other hand, Ga(I)is less stable than Ga(III), Ga(I) compounds behave as strong reducing agent.

5. Thus in *s*-block elements, groups 1 and 2 show only the group valency, while groups in *p*-block show variable valency, differing in steps of two. Variable valency also occurs with elements in the *d*-block. This arises from using different number of *d*-electron for bonding, so in this case the valence can change in steps of one (e.g. $Cu^{\oplus}$ and Cu^{2+}).

6. Gallium is apparently divalent in few compounds, such as $GaCl_2$. However, Ga is not really divalent, as the structure of $GaCl_2$ has been shown to be $Ga^{\oplus}[GaCl_4]^{\ominus}$ which contains Ga(I) and Ga(III).

Few important properties of thallium(I): Thallium(I) or thallous compounds are well known.

1. They are typically colourless.
2. They are extremely poisonous, when ingested in traces, turn the hair very black but in larger doses cause hair loss and death. Th(I) compounds are toxic as they upset the enzyme systems in the body.
3. In aqueous solution, Tl(I) ion is much more stable than Tl(III). The ionic radii of Tl ion (1.50 Å) is in between that of $K^{\oplus}$ ion (1.38 Å) and $Rb^{\oplus}$ ion (1.52 Å). Due to this, $Tl^{\oplus}$ resembles group 1 ions in a number of ways. Some points of resemblance are as follows:
   a. Both TlOH and Tl_2O are soluble in water and are strongly basic.
   b. They absorb CO_2 from the air to form Tl_2CO_3.
   c. The solublity of most Tl (I) salts are slightly lower than $K^{\oplus}$ salts. $Tl^{\oplus}$ ion can replace $K^{\oplus}$ ion in some enzymes, and th... ...ical tracer in the body.
   d. TlOH is yellow and on heating to 100°C, it turns into black Tl_2O.
   e. The coordination number for $Tl^{\oplus}$ is usually 6 or 8, as compared with 6 for group 1 ions.
   f. TlF is insoluble in water, but other halides are almost insoluble.

Thallium(I) resembles silver(I) too in the way, that like AgCl, TlCl is also sensitive to light and darkens when exposed to light, but TlCl is insoluble in NH_4OH while AgCl is soluble. **Trends in chemical reactivity:** Group 13 elements have three electrons in their valence shell. Apart from Tl, they normally use these to form three bonds and show an oxidation state of +3. These elements in +3 oxidation state are expected to form covalent compounds due to the following:

1. According to Fajans' rules, small size of the ions and high charge of +3, favour the formation of covalent bonds.
2. The sum of the first three ionisation enthalpies is very high and this also suggests that bonds will be largely covalent.
3. The electronegativity values of group 13 elements are higher than groups 1 and 2. On reacting with other elements the difference in electronegativity is not likely to be large.
4. The first ionisation enthalphy of B is 800 kJ mol^{-1}, which gives the impression that monovalent boron, $B^{\oplus}$, can be obtained. But in all the known compounds of boron it does not exist as $B^{\oplus}X^{\ominus}$ but as BX_3, a covalent compound. This is due to the fact that the energy released in the formation of $B^{\oplus}X^{\ominus}$ (ionic compound) is much less than the balance of the following:
   a. The energy needed to produce an sp^2 hybrid set of atomic orbitals
   b. The energy released in the formation of three covalent bonds in BX_3 compound

   This leads to more stable BX_3 (covalent compound) as compared to $B^{\oplus}X^{\ominus}$ (ionic compound).
5. Boron, due to its small size and high sum of the first three ionisation enthalpies does not form B^{3+} ion. Therefore, it does not form ionic compound and always form covalent compounds by sharing its valence electrons.
6. Many simple compounds of other elements such as $AlCl_3$, $GaCl_3$ and $InCl_3$ are covalent when anhydrous but in aqueous solution, these are ionic in nature. In anhydrous condition, the (charge/radius) ratio, i.e. polarisability of Al^{3+} is high and hence according to Fajans' rule, Al^{3+} polarises $Cl^{\ominus}$ ions to large extent, thereby introducing covalent character in the compound, i.e. $AlCl_3$ behaves as a covalent compound in anhydrous conditions. In aqueous medium, the ions get hydrated, because the amount of hydration enthalpy released exceeds the sum total of ionisation enthalpy required, i.e. to convert $Al \rightarrow Al^{3+}$, 5137 kJ mol^{-1} of ionisation enthalpy is required.

$\Delta H_{Hydration}$ for $Al^{3+} = -4865$ kJ mol^{-1}

$\Delta H_{Hydration}$ for $Cl^{\ominus} = -381$ kJ mol^{-1}

Total hydration enthalpy = [– 4865 × 3 (– 381)] kJ mol^{-1}

= – 5808 kJ mol^{-1}

Because the total hydration enthalpy exceeds ionisation enthalpy so $AlCl_3$ ionises in solution to give $[Al(H_2O)_6]^{3+}$ ions. Since the (charge/radius) ratio of hydrated aluminium ion is much smaller as compared to that of Al^{3+}, the tendency of $[Al(H_2O)_6]^{3+}$ to polarise hydrated $Cl^{\ominus}$ ion decreases and the resulting hydrated compound is ionic in nature.

7. The hydrated metal ions have six water molecules of crystallisation which are held very strongly in an octahedral structure $[M(H_2O)_6]^{3+}$. The metal oxygen bonds are very strong. This weakens the O–H bonds and the protons are released to neighbouring water molecules forming $H_3O^{\oplus}$ (hydrolysis).

$$[M(H_2O)_6]^{3+} + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{2+} + H_3O^{\oplus}$$

8. Ga, In and Tl apart from +3 oxidation state (group oxidation state) also exist in +1 oxidation state (due to inert pair effect). Since the (charge/radius) ratio of the ion in +1 oxidation state is smaller as compared to the ion in +3 oxidation state, tendency of $M^{\oplus}$ ion to polarise the anion will be less as compared to M^{3+} ion, therefore compound in which cation is in +1 oxidation state will be more ionic as compared to +3 oxidation state. MX will be more ionic as compared to MX_3, e.g. TlCl wil be more ionic as compared to $TlCl_3$.

6.5.2 Reactivity Towards Air

With dioxygen (O_2): All the group 13 elements react at high temperature forming trioxides, M_2O_3.

$$4M_{(s)} + O_{2(g)} \longrightarrow 2M_2O_{3(s)}$$

Tl, besides forming Tl_2O_3, also forms Tl_2O.

Down the group (↓), the reactivity of group 13 elements towards dioxygen increases.

Boron is unreactive in the crystalline form. However, finely divided amorphous boron reacts with dioxygen on heating to form B_2O_3.

$$4B_{(s)} + 3O_{2(g)} \xrightarrow{973\,K} 2B_2O_{3(s)}$$

Thermodynamically, Al should react with air, but it is stable. This is due to a very thin oxide film formed on the surface, which protects Al metal from further attack (this layer is only 10^{-4} to 10^{-6} mm thick). If the protective oxide layer is removed (for example by amalgamating with mercury) then the metal readily decomposes cold water forming Al_2O_3 and liberating H_2.

$$4Al_{(s)} + 3O_{2(g)} \xrightarrow{\Delta} Al_2O_{3(s)}$$

$$2Al_{(s)} + 3H_2O_{(l)} \longrightarrow Al_2O_{3(s)} + 3H_{2(g)}\uparrow$$

To give a decorative finish, aluminium articles are often 'anodised'. This is done by electrolysing dilute H_2SO_4 with Al as the anode. This produces a much thicker layer (10^{-2} mm) of oxide on the surface. This layer can take up pigments, thus colouring the aluminium.

With dinitrogen: N_2 at high temperature B and Al form corresponding nitrides, while Ga and In do not react.

$$2B_{(s)} + N_{2(g)} \xrightarrow{\text{High temp}} 2BN_{(s)}$$

$$2Al_{(s)} + N_{2(g)} \xrightarrow{\text{High temp}} 2AlN_{(s)}$$

6.5.3 Reactivity Towards Acids and Alkalis

Boron does not react with non-oxidising acids such as HCl. However, at high temperature it reacts with strong oxidising acids such as mixture of hot conc H_2SO_4 and HNO_3 (2:1) to give boric acid.

$$B_{(s)} + 3HNO_{3(aq)} \xrightarrow[\Delta]{H_2SO_4} \underset{\text{Boric acid}}{H_3BO_{3(aq)}} + 3NO_{2(g)}$$

Boron resists the action of alkalis (NaOH or KOH) upto 773 K, but above 773 K, boron forms borates.

$$2B_{(s)} + 6KOH_{(s)} \xrightarrow{>773\,K} \underset{\text{potassium borate}}{2K_3BO_{3(s)}} + 3H_{2(g)}$$

B also dissolves in fused $Na_2CO_3/NaNO_3$ mixture at 1123 K.

$$2B_{(s)} + 3NaCO_{3(s)} + 3NaNO_{3(s)} \longrightarrow 2Na_3BO_{3(s)} + 3NaNO_{3(s)} + 3CO_{2(g)}$$

All other elements react both with non-oxidising and oxidising acids. For example, Al reacts with dilute acids liberating H_2 gas.

$$2Al_{(s)} + 6HCl_{(g)} \longrightarrow 2Al^{3+}_{(aq)} + 6Cl^{\ominus}_{(aq)} + 3H_2\uparrow_{(g)}$$

However, conc HNO_3 renders Al and Ga passive by forming a thin protective layer of oxide (Al_2O_3 or Ga_2O_3) on the surface which prevents it from further attack.

Al and Ga also dissolve in alkalis with the evolution of H_2 gas.

$$2Al_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(l)} \longrightarrow \underset{\text{Sodium tetrahydroxoaluminate(III)}}{2Na^{\oplus}[Al(OH)_4]^{\ominus}_{(aq)}} + 3H_{2(g)}$$

$$2Ga_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(l)} \longrightarrow 2Na^{\oplus}[Ga(OH)_4]^{\ominus}_{(aq)} + 3H_{2(g)}$$

Since all other elements (except B) of group 13 react both with acid and base these are amphoteric in nature.

6.5.4 Reactivity Towards Halogens

Group 13 elements react with halogens at high temperature to form trihalides having general formula, MX_3.

$$2M_{(s)} + 3X_{2(g)} \xrightarrow{\Delta} 2MX_3 \quad (\text{where } X = F, Cl, Br, I)$$

All possible halides have been prepared for all group 13 elements except thallium, for which only thallium trifluoride (TlF_3), thallium trichloride ($TlCl_3$) and thallium tribromide ($TlBr_3$) have been obtained. $TlCl_3$ and $TlBr_3$ tend to lose halogens and revert to Tl(I) state. This is due to oxidising character of Tl(III) state coupled with the reducing character of $Cl^{\ominus}$ and $Br^{\ominus}$. TlI_3 does not exist due to oxidising character of Tl(III) and strong reducing character of $I^{\ominus}$ ion,

$$TlCl_3 \longrightarrow TlCl + Cl_2\uparrow$$

$$TlBr_3 \longrightarrow TlBr + Br_2\uparrow$$

6.5.5 Reactivity Towards Water

Boron is not at all affected by water or steam. However, at red heat steam reacts.

$$2B + \underset{\text{Steam}}{3H_2O} \xrightarrow{\text{Red heat}} B_2O_3 + 3H_2$$

Aluminium decomposes cold water if the oxide layer is not present on its surface.

$2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2\uparrow$

Gallium and indium are not attacked by cold or hot water unless oxygen is present. Thallium forms TlOH in moist air.

$4Tl + 2H_2O + O_2 \longrightarrow 4TlOH$

6.5.6 Reactivity Towards Metals

Boron combines with metals on heating to form borides. The rest of the elements do not combine with metals. This shows boron is a non-metal and rest of the elements are metals.

$3Mg + 2B \longrightarrow Mg_3B_2$

6.5.7 Complex Forming Tendency

Group 13 elements form complexes much more readily than group 1 and group 2 elements (collectively known as *s*-block elements) due to their smaller size and increased charge.

Alkali metal borohydrides such as $LiBH_4$ and $NaBH_4$ are examples of well known complexes of boron. These contain the complex $[BF_4]^{\ominus}$ which is formed by the sp^3 hybridisation of orbitals of boron. It is therefore has tetrahedral geometry.

Several other tetrahedral complexes which are formed by other group 13 elements are also well known, e.g. $Li[AlH_4]$, $NH_4[AlF_4]$ etc.

In addition to the above tetrahalides and tetrahydrides, many octahedral complexes such as $[GaCl_6]^{3-}$, $[InCl_6]^{3-}$, $[TlCl_6]^{3-}$ etc. are known. The most important octahedral complexes are those which are formed with chelate groups, for example oxalate ions, dicarboxylic acid, β-diketone such as acetylacetone, 8-hydroxyquinoline. 8-Hydroxyquinoline is used in the gravimetric estimation of aluminium.

6.6 GENERAL CHARACTERISTICS OF THE COMPOUNDS OF GROUP 13 ELEMENTS

6.6.1 Oxides and Hydroxides

All the elements of group 13 form sesquioxides, M_2O_3 ('*Sesqui*' means one and a half, so the oxide should have formula $MO_{1.5}$ or M_2O_3). Boron forms B_2O_3 as well as a suboxide $(BO)_x$. B_2O_3 exists in two forms: glassy and crystalline. Glassy B_2O_3 is obtained by the following:

1. Heating amorphous boron in air

$$\underset{\text{Amorphous}}{4B} + \underset{\text{(Air)}}{3O_2} \longrightarrow 2B_2O_3$$

2. By dehydrating H_3BO_3

$$H_3BO_3 \xrightarrow[-H_2O]{100°C} \underset{\text{Meta-boric acid}}{HBO_2} \xrightarrow[-H_2O]{\text{Red heat}} \underset{\text{Glassy}}{B_2O_3}$$

B_2O_3, boric oxide, is actually an anhydride of orthoboric acid.

Crystalline B_2O_3 has been obtained by dehydrating HBO_2 by keeping it under reduced pressure and slowly raising the temperature to 400°C over a period of several weeks.

$$H_3BO_3 \xrightarrow[-H_2O]{100°C} HBO_2 \xrightarrow[\text{Reduced pressure}]{400°C} \underset{\text{Crystalline}}{B_2O_3}$$

In glassy B_2O_3, there exist randomly oriented three-dimensional networks of BO_3 groups, each oxygen being bonded to two boron atoms.

The structure of crystalline B_2O_3, consists of BO_4 tetrahedra, two sets of which form two types of interconnected spiral chains, three B–O bonds are equivalent, but the fourth one is somewhat longer.

Boron suboxide $(BO)_2$ is obtained by heating B_2O_3 with boron at 1050°C.

$$B + B_2O_3 \xrightarrow{1050°C} (BO)_2$$

The structure of the solid compound is unknown.

The oxides of Al, Ga, In and Tl may all be prepared by the thermal decomposition of their nitrates or hydroxides.

$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$

Stoichiometrically, there is only one oxide of aluminium, Al_2O_3, commonly known as alumina. It occurs in nature in various forms. The most common forms are

- α-Al_2O_3 also known as '*corundum*'
- γ-Al_2O_3 also known as '*activated alumina*'

The so-called β-Al_2O_3 is not pure Al_2O_3, rather it has the composition, $Na_2O \cdot Al_2O_3$.

6.6.1.1 α-Al_2O_3

1. It has a well-defined closed packed structure of oxygen atoms with Al^{3+} occupying octahedral holes.
2. α-form of Al_2O_3 is the fourth hardest substance known, being exceeded only by diamond, boron nitride and carborundum.
3. It is stable at high temperature.
4. It dissolves both in acids and alkalis.
5. In certain instances, traces of transition metal oxides give substances that are classified as gem stones.
   a. Ruby (red) is α-Al_2O_3 containing a trace of Cr^{3+}.
   b. Blue sapphire contains Fe^{2+} and Tl^{4+}.
   c. Mixtures of Al_2O_3 and certain other metallic oxides on molar basis also give products that are of gem quality, e.g. alexandrite ($Al_2O_3 \cdot BeO$) and spinel ($Al_2O_3 \cdot MgO$).

6.6.1.2 γ-Alumina

1. γ-Alumina has a distorted, badly organised, micro-crystalline structure of spinel type.
2. γ-Al_2O_3 is metastable and not found in nature but can be prepared by carefully heating $Al(OH)_3$ up to 400°C.
3. It is characterised by small particle size of high surface area.
4. γ-Al_2O_3 on prolonged heating at 1000°C form α-Al_2O_3.
5. It readly takes up water and dissolve in acids.

The Al_2O_3 which forms on the surface of the aluminium metal has still another structure, namely a defect rock salt structure, there is an arrangement of Al and O ions in the rock salt ordering with every third Al^{3+} ion missing.

The properties of Ga_2O_3 follow closely those of Al_2O_3. A stable temperature form (α-Ga_2O_3) and a metastable low temperature form (γ-Ga_2O_3) exist. The crystal structures of these two forms of Ga_2O_3 follow the same pattern as described for the corresponding aluminium oxides.

Yellow indium oxide (In_2O_3) and dark-coloured thallium oxide (Tl_2O_3) are known only in one form. Thallium trioxide readily lose oxygen at about 100°C to give thallous oxide (Tl_2O).

$$Tl_2O_3 \xrightarrow{100^\circ C} Tl_2O + O_2 \uparrow$$

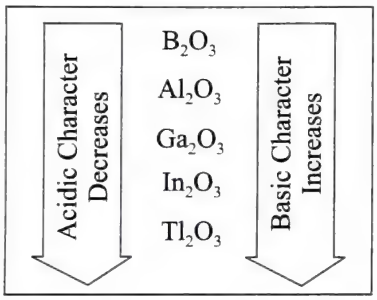
6.6.2 Acid–Base Behaviour

Down the group (↓), there is a gradual change from acidic to amphoteric and then to basic character of oxides.

$$\underset{\text{More acidic less basic}}{B_2O_3} \quad \underbrace{Al_2O_3 \quad Ga_2O_3}_{\text{Amphoteric}} \quad \underbrace{In_2O_3 \quad Tl_2O_3}_{\text{Basic}}$$

Down the group (↓), the acidic character of the oxides decreases and the basic character increases.

This is due to decrease in ionisation enthalpy down the group (↓). As a result, M–O bond weakens and is easily dissociated, thereby the basic strength increases.



B_2O_3 is weakly acidic and combines with alkalis and metal oxides to form basic metaborates.

$$B_2O_3 + 2NaOH \longrightarrow \underset{\text{Sodium metaborate}}{2NaBO_2} + H_2O$$

$$B_2O_3 + CuO \longrightarrow Cu(BO_2)_2$$

$$B_2O_3 + CoO \longrightarrow Co(BO_2)_2$$

B_2O_3 also reacts with very strong acidic oxides like P_4O_{10} and As_4O_{10} to form phosphates and arsenates respectively. Hence, it behaves as basic oxide.

$$2B_2O_3 + P_4O_{10} \longrightarrow 4BPO_4$$

$$2B_2O_3 + As_4O_{10} \longrightarrow 4BAsO_4$$

Oxides of Al and Ga, i.e. Al_2O_3 and Ga_2O_3 respectively are amphoteric and hence dissolve both in acids and in bases forming salts.

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

$$Al_2O_3 + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + H_2O$$

$$2Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

$$Ga_2O_3 + 6HCl \longrightarrow 2GaCl_3 + 3H_2O$$

$$Ga_2O_3 + H_2SO_4 \longrightarrow Ga_2(SO_4)_3 + H_2O$$

$$2Ga_2O_3 + 2NaOH \longrightarrow 2NaGaO_2 + H_2O$$

Oxides of In and Tl, i.e. In_2O_3 and Tl_2O_3 respectively are basic in nature.

$$Tl_2O_3 + 3H_2SO_4 \longrightarrow Tl_2(SO_4)_3 + 3H_2O$$

Thallium also forms Tl_2O (due to inert pair effect, +1 oxidation state is more stable as compared to +3) and behaves as an alkali metal oxide. $Tl_2O + H_2O \longrightarrow 2TlOH$

The acid–base behaviour of M_2O_3 can also be explained as follows:

In B_2O_3, due to small size of B, positive charge density on B-atom is high. This pulls off electrons from H_2O molecules resulting in the weakening of O–H bond and therefore facilitates the release of proton giving acidic solution. As Al^{3+} and Ga^{3+} have relatively larger size as compared to boron, the positive charge density decreases, and their tendency to break the O–H bond becomes somewhat less. Due to this, the acidic nature decreases and the oxides become amphoteric. In^{3+} and Tl^{3+} are even larger and their interaction with water is negligible, hence their oxides are basic in nature.

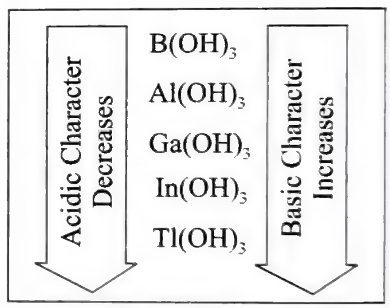
The trioxides of group 13 elements, M_2O_3, react with water to form the corresponding hydroxides.

$$M_2O_{3(s)} + 3H_2O \longrightarrow 2M(OH)_3$$

Down the group (↓), there is a gradual change from acidic to amphoteric and then to basic character of the hydroxides.

$$\underset{\text{Acidic}}{B(OH)_3} \quad \underbrace{Al(OH)_3 \quad Ga(OH)_3}_{\text{Amphoteric}} \quad \underbrace{In(OH)_3 \quad Tl(OH)_3}_{\text{Basic}}$$

Down the group (↓), the acidic character of the hydroxides decreases and the basic character increases.



The change in acidic to basic character can be explained in similar way as explained in the case of oxide of group 13 elements. $B(OH)_3$ acts as acid in aqueous medium. $B(OH)_3$ coordinates with H_2O molecule to form

$$\left[(HO)_3B \leftarrow :O\begin{matrix} H \\ H \end{matrix}\right]$$

B^{3+} pulls the electron charge of O-atom towards itself. The coordinated O-atom, in turn pulls the electron pair of O–H towards itself, which facilitates the cleavage of O–H bond, thereby releasing $H^{\oplus}$ ion. The aqueous solution of $B(OH)_3$ acts as a weak acid.

$$B(OH)_3 + H_2O \rightleftharpoons [B(OH)_4]^{\ominus} + H^{\oplus}$$

As the size of the central ion increases, the positive charge density on central ion decreases and hence the tendency to break O–H bond decreases. Down the group (↓), therefore the acidic character decreases or basic character increases.

$Al(OH)_3$ and $Ga(OH)_3$ are amphoteric and hence dissolve in acids as well as bases.

$$Al(OH)_3 + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 6H_2O$$

$$Al(OH)_3 + 2NaOH \longrightarrow NaAlO_2 + H_2O \text{ or } Na^{\oplus}[Al(OH)_4]^{\ominus}$$

$$Ga(OH)_2 + H_2SO_4 \longrightarrow Ga_2(SO_4)_3 + 6H_2O$$

$$Ga(OH)_3 + 2NaOH \longrightarrow NaGaO_2 + H_2O \text{ or } Na^{\oplus}[Ga(OH)_4]^{\ominus}$$

6.6.3 HYDRIDES

Group 13 elements do not combine directly with hydrogen. However, a number of hydrides are known. Boron with hydrogen forms a number of boron hydrides also known as boranes by analogy with alkanes (hydrocarbon). From their position in the periodic table, group 13 elements would be expected to form the simplest hydride having the stoichiometric formula, MH_3.

For boranes, the compound BH_3 is not known because hydrogen atom in BH_3 does not have a pair of electron to form B–H $p\pi$–$p\pi$ bond and compensate for the electron deficiency of boron. Thus, boron in BH_3 will have incomplete octet and BH_3 will not exist. Instead, BH_3 dimerises to form B_2H_6 having both (2*c*, 2*e*) and (3*c*, 2*e*) bonds. Boranes are electron-deficient compounds.

Although there is some evidence for the existence of AlH_3 and Al_2H_6 in the gas phase at low pressure. The only stable binary hydride of aluminium is *alane* $(AlH_3)_n$ which is obtained as a white powder by the reaction of aluminium chloride with lithium hydride in ether solution.

$$Al_2Cl_6 + 6LiH \xrightarrow{\text{Ether}} (AlH_3)_n + LiCl$$

If excess LiH is used in the preparation, a compound containing the aluminohydride is obtained.

$$LiH + AlH_3 \longrightarrow \underset{\text{Lithium aluminium hydride}}{LiAlH_4}$$

Boron and gallium also form complex anionic hydrides. These act as strong reducing agents.

$NaBH_4$ Sodium borohydride

$LiGaH_4$ Lithium gallium hydride

Gallium forms a dimeric hydride, digallane, Ga_2H_6. Indium forms a polymeric hydride, $(InH_3)_n$. Thallium does not form any hydride.

6.6.4 HALIDES

Group 13 elements form a number of trihalides as well as lower halides.

Trihalides, MX_3: All the elements of group 13 form trihalides.

Trihalides of boron:

1. BF_3 is a colourless gas (b.pt. 172 K), BCl_3 and BBr_3 are colourless liquids (b.pt. 285 K and 363 K respectively) and BI_3 is a white solid (m.pt. 316 K).
2. Due to small size and high ionisation enthalpy of boron the trihalides formed by boron are covalent in nature.
3. All these trihalides are planar molecules (Fig. 6.2), with $\angle XBX = 120°$. In BX_3, B is sp^2 hybridised.

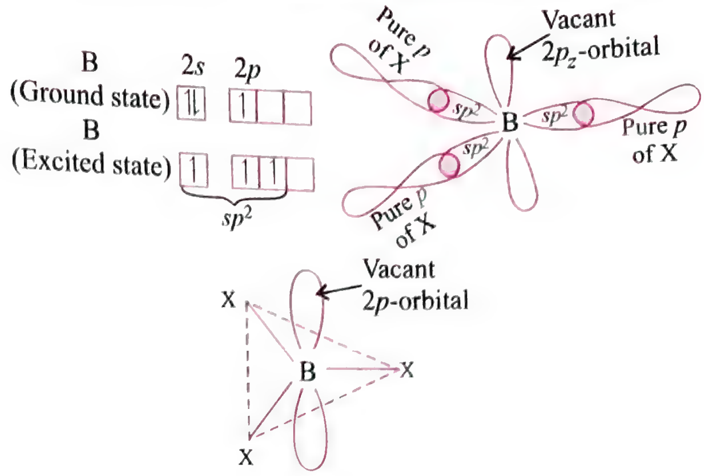


Fig. 6.2 Structure of boron trihalides, BX_3

The three half-filled *p*-orbitals, one on each halogen, overlap alongwith their internuclear axis with three sp^2 hybridised orbitals of boron to form three sp^2-*p*, B–X (σ) bonds. The unhybridised $2p_z$ orbital on B, however remains empty.

B-atom in BX_3 has only six electrons in its valence shell, that is why these compounds are *electron- deficient compounds*, and behave as Lewis acids.

4. The bond length in trihalides (BX_3) is somewhat shorter than would be expected for single electron pair. The electron deficiency in BX_3 is reduced by back donation of an electron pair from filled np_z orbital of halogen atom to the vacant $2p_z$ orbital on B-atom, thus a double bond is established between B and X atoms, due to $p\pi$–$p\pi$ back bonding.

If one localised double bond existed, there would be one short and two longer B–X bonds. However, all the three B–X bond lengths are equal and this is explained on the basis of resonance between the three structures with double bond in different positions (Fig. 6.3).

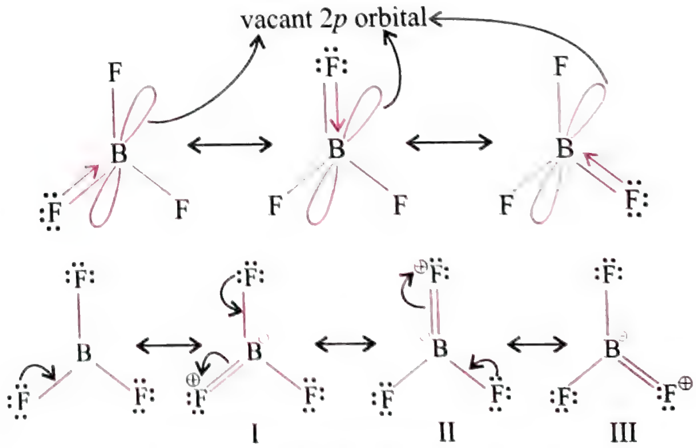
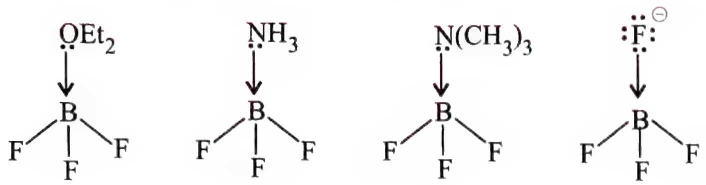


Fig. 6.3 Resonating structure of BF_3 molecule

Since BX_3 are electron-deficient compounds, they behave as *Lewis acids*. The empty $2p_z$ orbital on B-atom in BF_3 can accept a lone pair of electron from donor molecules such as Et_2O, NH_3 and $(CH_3)_3N$ or by ions such as $F^{\ominus}$. When this occurs, the geometry of the compound changes from planar triangle to tetrahedral.



Once a tetrahedral complex has been formed, the possibility of $p\pi$–$p\pi$ bonding no longer exists. The B–F bond distance in $[F_3B \leftarrow : NH_3]$ is 1.38 Å and in $[F_3B \leftarrow : N(CH_3)_3]$ is 1.39 Å which is much longer than 1.30 Å in BF_3.

6.6.5 Relative Strengths of Trihalides of Boron as Lewis Acids

The relative strength of trihalides of boron to accept a pair of electron and thus to behave as Lewis acid has been found to decrease in the order: $BF_3 < BCl_3 < BBr_3$.

The order is just the reverse of what should be expected normally from the electronegativities of the halogen. Since the electronegativity of the halogens follow the order: F > Cl > Br. Therefore, the Lewis acid strength order should be: $BF_3 > BCl_3 > BBr_3$.

This anomalous behaviour can be explained on the basis of the tendency of the halogen atom to back donate its electron pair from filled np_z orbital to the vacant $2p_z$ orbital of central B-atom, thus resulting in $p\pi$–$p\pi$ back bonding (Fig. 6.4).

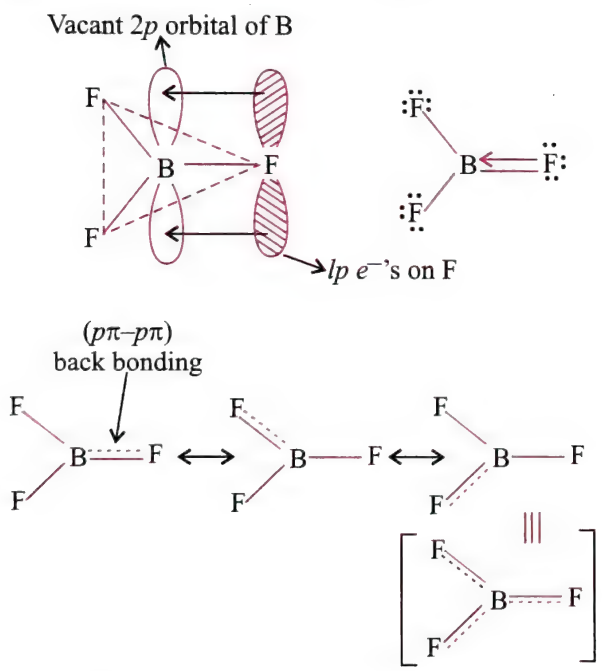


Fig. 6.4 $p\pi$–$p\pi$ **back-bonding in** BF_3 **moloecule**

In BF_3, an electron pair is donated from filled $2p_z$ orbital of F to the vacant $2p_z$ orbital of B for the $p\pi$–$p\pi$ bond formation. An effective overlap is easily possible as both the orbitals have identical size and belong to same energy level. In other words, an additional $p\pi$–$p\pi$ bond in BX_3 is supported by the fact that the observed B–F bond length in BF_3 is 1.30 Å, which is significantly shorter than the expected B–F radii (sum of the covalent radii of B and F, which are 0.80 Å and 0.72 Å respectively). The bond enthalpy is very high, i.e. 646 kJ mol^{-1}, which is higher than for any single bond (Table 6.4).

Table 6.4 Structural parameters for boron trihalides, BX_3

Compound	∠XBX	d(B–X) observed (Å)	Calculated or expected* d(B–X) (Å)
BF_3	120°	1.30	1.52
BCl_3	120°	1.76	1.87
BBr_3	120 ± 6°	1.87	1.94

* Based on the summation of covalent radii, $r_B = 0.80$ Å, $r_F = 0.72$ Å, $r_{Cl} = 1.07$ Å, $r_{Br} = 1.14$ Å.

The shortness and strength of the bonds are interpreted in terms of $p\pi$–$p\pi$ back bonding. The empty $2p_z$ orbital on B, which is not involved in hybridisation is perpendicular to the planar triangle containing the sp^2 hybrid orbitals. This $2p_z$ orbital on B may accept an electron pair from filled p_z orbital on any one of three X-atoms. Thus, a dative π bond is formed, and the B atom attains an octet of electron. Due to $p\pi$–$p\pi$ bond formation, the bonds possess some double bond character, resulting in shortening and strengthening of the bond (Fig. 6.4). The B–F bond thus acquires some double bond character (Fig. 6.4). This type of bond formation is known as back bonding. As a result of $p\pi$–$p\pi$ back bonding, the electron deficiency of boron in BF_3 decreases and thus, the Lewis acid character of BF_3 decreases. As the size of halogen atom increases from F to Cl to Br, the extent of overlap between vacant $2p$ orbital of boron and filled $3p$ orbital of Cl or $4p$ orbital of Br decreases, due to appreciable differences in the energies of the overlapping orbitals. Hence, the tendency of $p\pi$–$p\pi$ bond formation decreases in the order: $BF_3 > BCl_3 > BBr_3$. As a result, the electron deficiency of B is reduced to a maximum extent in $BF_3 > BCl_3 > BBr_3$. Thus, the tendency of BF_3 to accept a pair of electron and to behave as Lewis acid is least while that of BI_3 is maximum. Thus, the relative order of Lewis acid strength is $BF_3 < BCl_3 < BBr_3$.

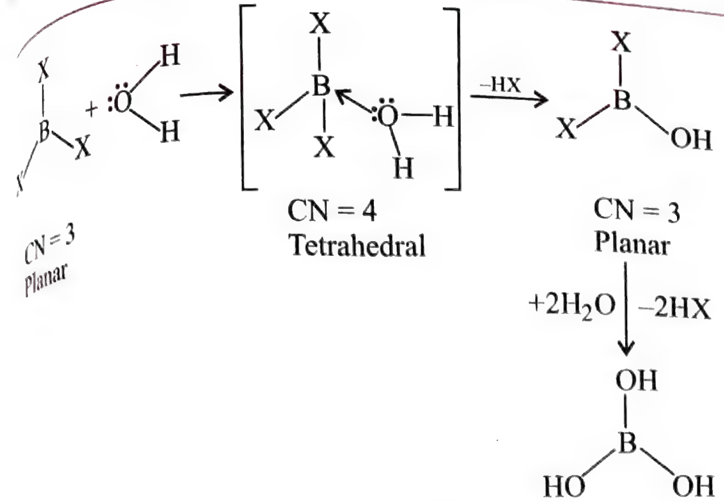
All the boron halides are hydrolysed by water. BF_3 hydrolyse incompletely to form fluoroborates. This is because the HF formed first reacts with $B(OH)_3$.

$$4BF_3 + 12H_2O \longrightarrow 4H_3BO_3 + 12HF$$
$$12HF + 3H_3BO_3 \longrightarrow 3H^{\oplus} + 3[BF_4]^{\ominus} + 9H_2O$$
$$4BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3H^{\oplus} + 3[BF_4]^{\ominus}$$

Higher halides do not react with H_3BO_3, possibly due to lower stability of $[BCl_4]^{\ominus}$ or $[BBr_4]^{\ominus}$ or $[BI_4]^{\ominus}$ ion.

$$BX_3 + 3H_2O \longrightarrow H_3BO_3 + 3HX \qquad \text{(where X = Cl, Br, I)}$$

The hydrolysis proceeds as follows:



B in BX_3 has vacant $2p$ orbital in which it accepts a pair of electron from O-atom of H_2O molecule, thus forming a tetrahedral intermediate addition compound. Further, elimination of HX molecule takes place and B–OH bond is formed. This process goes on resulting in the formation of $B(OH)_3$.

Hydrolysis trend: $BF_3 < BCl_3 < BBr_3$

As the Lewis acid character decreases in the order: $BF_3 < BCl_3 < BBr_3$, tendency to get hydrolysed also varies in the same order: $BF_3 < BCl_3 < BBr_3$.

The trifluorides of Al, Ga, In and Tl are non-volatile, ionic solids with high melting points. These are slightly soluble in water.

Chlorides, bromides and iodides of Al, Ga, In and Tl are largely covalent. They are relativity volatile and the vapours consist of dimeric molecules. They readily dissolve in non-polar solvents like benzene, in which they are present as dimers. The anhydrous trichlorides fume in most air due to hydrolysis.

$$MCl_3 + 3H_2O \longrightarrow M(OH)_3 + \underset{\text{(Fumes)}}{3HCl\uparrow}$$

The tribromides and triodides are also hydrolysed.

The unusually high melting points of AlF_3, GaF_3 and InF_3 suggest that these compounds exist as three-dimensional giant molecules. AlF_3 differs from other halides of Al in being non-volatile and insoluble. The differences may be correlated to the change in coordination number of Al which is 6 for AlF_3, changes from 6 to 4 at the melting point for $AlCl_3$ and is 4 for $AlBr_3$ and AlI_3.

In AlF_3, each Al^{3+} ion is surrounded by six $F^{\ominus}$ ions in a distorted octahedral arrangement; each F acts as a bridge between two octahedra (Fig. 6.5), thus giving the stoichiometry as 1:3.

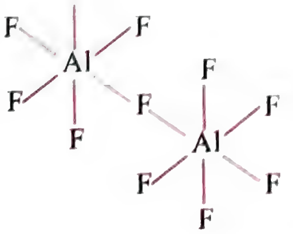


Fig. 6.5 Structure of AlF_3 (solid)

In solid $AlCl_3$, Al is octahedrally coordinated, i.e. has six coordination number and two Cl atoms in each octahedra are shared between Al atoms (Fig. 6.6).

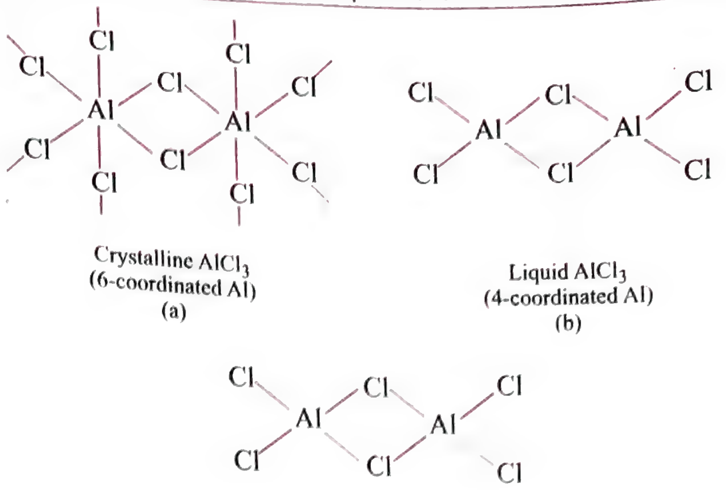


Fig. 6.6 (a) Structure of crystalline $AlCl_3$, (b) liquid $AlCl_3$ and (c) $AlCl_3$ in vapour phase

$InCl_3$ and $TlCl_3$ in the solid state have a similar structure. At the melting point of $AlCl_3$ (465 K), the structure [Fig. 6.6 (a)] changes to four-coordinate molecular dimer Al_2Cl_6 [Fig. 6.6 (b)] as a result the volume decreases to about 85% and the electrical conductivity drops almost to zero. In the gaseous phase, at lower temperatures, the covalently bonded molecular dimers are the main species [Fig. 6.6 (c)], but at higher temperatures monomers are formed which are believed to be trigonal planar $AlCl_3$ molecules isostructural with BX_3.

The halides with coordination number 4, i.e. AlX_3, where X = Br, I; GaX_3, where X = Cl, Br, I; InX_3, where X = I and TlX_3, where X = Br, form dimeric molecular units in the crystalline phase as well as in the liquid and vapour phase (Fig. 6.7).

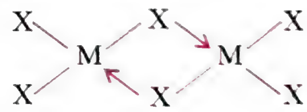


Fig. 6.7 Structure of M_2X_6

Thallium trichloride ($TlCl_3$) and thallium tribromide ($TlBr_3$) are unstable and disproportionate to the monohalide and halogen.

$$TlX_3 \xrightarrow{\text{Disproportionation}} TlX + X_2 \qquad \text{(where X = Cl, Br)}$$

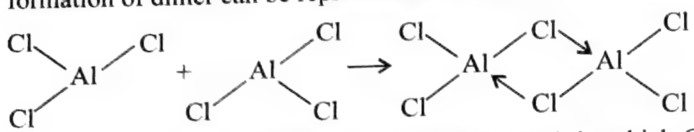
TlI_3 is correctly formulated as $Tl^{\oplus}(I_3)^{\ominus}$ and not as $Tl^{3+}(I^{\ominus})_3$. TlI_3 is isomorphous with CsI_3, therefore it contains the linear tri-iodide ion, $I_3^{\ominus}$ and is infact a compound of Tl(I). Further, from the standard reduction potentials, $E^{\ominus}(Tl^{3+}/Tl^{\oplus}) = +1.25$ V and $E^{\ominus}(I/2I_2/I^{\ominus}) = +0.54$ V, it is clear that Tl(III) is completely reduced to Tl(I) in acid solution.

Like the boron halides, the halides of other group 13 elements also behave as Lewis acids. The Lewis acid character decreases as the size of the cation increases. Four coordinate-addition compounds of the type, $L{:}MX_3$ are formed, where L is Lewis base. These four coordinate species have a tetrahedral arrangement of atoms and probably involves the use of sp^3 hybrid orbitals in bonding. Coordination number greater than 4 may also be achieved by using d-orbitals. Complexes such

$[MY_6]^{3-}$ are known in which the metal is present in an octahedral environment of lower halides.

6.6.6 Characteristic Differences in the Structures of Boron Trihalides and Aluminium Trihalides

Boron trihalides exist as monomers, whereas aluminium trihalides exist as dimers. For example, $AlCl_3$ exists as a dimer, Al_2Cl_6, in non-polar solvents as well as in vapour state between 400° and 800°C. Above 800°C, however it exists as a monomer. The formation of dimer can be represented as follows:



The arrows indicate formation of a dative bond, in which Cl donates an electron pair to Al. The covalency of Al increases to 4. The chlorine atoms are tetrahedrally arranged around each Al atom. Such bridge structures are typical of electron-deficient compounds.

Boron trihalides, however, do not form dimers. They exist only as monomers. This is due to the fact that boron atom is too small to coordinate with four large halide ions such as $Cl^{\ominus}$, $Br^{\ominus}$ and $I^{\ominus}$. However, B-atoms should be able to coordinate with $F^{\ominus}$ ions which are much smaller in size than other halide ions. Consequently, of the various boron trihalides, BF_3 should at least exist as a dimer. But actually, it is not so. This is due to the large amount of energy required for the cleavage of $p\pi$–$p\pi$ bond in BF_3 to enable dimerisation of BF_3, is not released during the bridge structure in this case. Therefore, BF_3 can exist only as a monomer as do the other halides of boron.

6.6.7 Lower Halides of Boron

Diboron tetrahalide, B_2X_4, where X = F, Cl, Br, I are well known. These dihalides are thermally less stable than the corresponding BX_3 and decomposes into B and BX_3. B_2F_6, the most stable out of these, decomposes at the rate of about 8% per day at room temperature. The thermal stability of diboron tetrahalides varies with the extent of $p\pi$–$p\pi$ back bonding between B and X. Thus B_2F_4, which has a planar structure with maximum possibility of $p\pi$–$p\pi$ bonding is more stable than B_2Cl_4 which has a staggered structure.

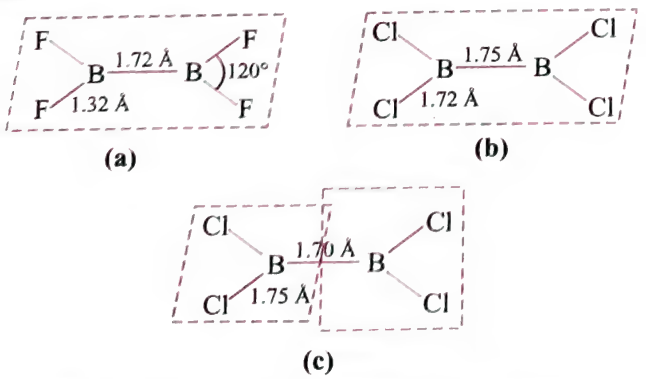


Fig. 6.8 (a) B_2F_4, (b) B_2Cl_4 solid and (c) B_2Cl_4 vapour

In the solid state, B_2Cl_4 is a planar molecule, whereas in vapour state, the two BCl_2 units are at right angles to each other (Fig. 6.8).

6.6.8 Lower Halides of Al, Ga, In and Tl

Al, Ga, In and Tl form monohalides, MX. Those of Al, Ga and In are unstable and have reducing properties. AlF being most unstable, undergoes quick disproportionation into Al and AlF_3.

$$3AlF \longrightarrow 2Al + AlF_3$$

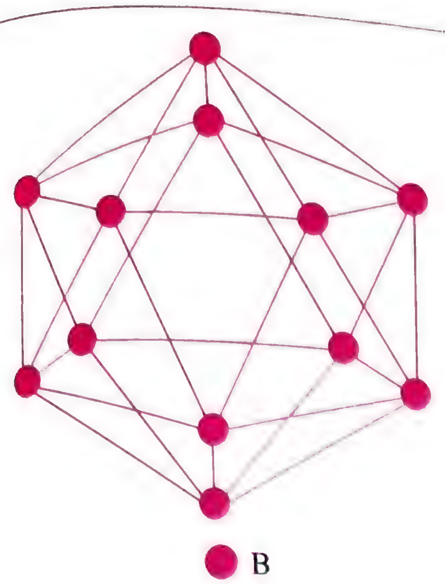
Other monohalides, also decompose, though less quickly in a similar way.

For a particular element of group 13, the monohalides of other halogens are more stable than the monofluoride, i.e. GaCl, GaBr, GaI are thermodynamically more stable than GaF. The stability of gallium(I) halide increases with an increase in the size of the halide ion. Gallium forms dihalides of the composition, GaX_2, which are actually salts of Ga(I). $GaCl_2$ or Ga_2Cl_4 is actually a mixed halide of Ga(I) and Ga(III) and its correct formula is $\overset{I}{Ga}[\overset{III}{Ga}Cl_4]$. Similarly, indium(I) chloride, indium(I) bromide and indium(I) iodide are thermodynamically more stable than indium(I) fluoride. The chloride of indium, In_2Cl_3, appears to have In in the 1.5 oxidation state, but actually it contains both In(I) and In(III) ion, and is correctly formulated as $\overset{I}{In_3}[\overset{III}{In}Cl_6]$. Thallium(I) halides are the most stable among the monohalides of group 13 elements. Several lower halides of Tl are known, e.g. $TlCl_2$, $TlBr_2$, Tl_2Cl_3, Tl_2Br_3. All these are mixed halides of Tl(I) and Tl(III).

6.7 BORON

6.7.1 Physical Properties of Boron

1. Boron is an extremely hard, black coloured, low density solid. Its melting point is very high (2453 K) and volatilises appreciably even at 1873K.
2. Boron is non-metallic in nature and has low electrical conductivity.
3. Elemental boron exists in several different modifications. The phenomenon of existence of different forms of an element is called ALLOTROPY. At least four different allotropes of boron may be obtained under different conditions. However, the transition between different forms is an extremely slow process. All boron allotropes have structures built up of B_{12} icosahedral units shown in Fig. 6.9.



Salient features of icosahedron:
a. 20 faces (equilateral triangle)
b. 12 corners
c. 30 edges
d. 5 boron atoms are equidistant from the given B-atom
e. There are some (3c, 2e) bonds

Fig. 6.9 The B_{12} icosahedral unit, the basic building block of the structure of allotrope of boron

6.7.2 Chemical Properties of Boron

The chemical reactivity of boron depends markedly on the state of its subdivision and temperature.

1. **Reaction with air:** Amorphous form when heated in air at 700°C, burns with a reddish flame forming a mixture of boric anhydride (B_2O_3) and boron nitride (BN).

   $4B + 3O_2 \longrightarrow 2B_2O_3$ (Basic anhydride)

   $2B + N_2 \xrightarrow{\Delta} 2BN$ (Boron nitride)

2. **Reaction with water:** Under ordinary conditions, boron is not affected by water, but when steam is passed over red hot boron, hydrogen is liberated.

   $$2B + 3H_2O \longrightarrow \underset{\text{Boric anhydride}}{B_2O_3} + 3H_2O\uparrow$$

3. **Reaction with acids:** Boron is very inert and is attacked by strong oxidising agents like conc HNO_3, but is not affected by non-oxidising acids like HCl.

   $2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2\uparrow$

   $B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2\uparrow$

4. **Reaction with alkalis:** Boron reacts with fused alkali metal hydroxides forming borates and evolving hydrogen.

   $2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2\uparrow$

5. **Reaction with metals:** Boron combines with strong electropositive metals at high temperatures to form borides, often non-stoichiometric.

   $3Mg + 2B \longrightarrow Mg_3B_2$

6. **Reaction with non-metals:** At higher temperature, boron reacts with almost all non-metals except hydrogen and noble gases.

   a. Boron combines with nitrogen when heated in air to form boron nitride (BN).

   $2B + N_2 \longrightarrow 2BN$

   b. Boron combines with carbon at high temperature to give boron carbide (B_4C).

   $4B + C \longrightarrow B_4C$

   B_4C is used in bulletproof clothings.

   c. Boron combines with halogens at high temperatures to yield covalent boron trihalides, e.g. BF_3, BCl_3.

   $2B + 3X_2 \longrightarrow 2BX_3$ (where X = F, Cl, Br, I)

7. Boron is a powerful reducing agent.

   $4B + 3CO_2 \longrightarrow 2B_2O_3 + 3C$

   $4B + 3SiO_2 \longrightarrow 2B_2O_3 + 3Si$

Some reactions of amorphous boron and of other group 13 elements (except B) are given in Tables 6.5 and 6.6, respectively.

Table 6.5 Some reactions of amorphous boron

Reaction	Remark
$4B + 3O_2 \longrightarrow 2B_2O_3$	• At high temperature
$2B + 3S \longrightarrow B_2S_3$	• At 1200°C
$2B + 2N_2 \longrightarrow 2BN$	• At very high temperature
$2B + 3F_2 \longrightarrow 2BF_3$ $2B + 3Cl_2 \longrightarrow 2BCl_3$ $2B + 3Br_2 \longrightarrow 2BBr_3$ $2B + 3I_2 \longrightarrow 2BI_3$	• At high temperature
$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$	• When fused with alkali
$2B + 2NH_3 \longrightarrow 2BN + 3H_2$	• At very high temperature
$B + M \longrightarrow M_xB_y$	• Many metals form borides (excluding group 1), which are often non-stoichiometric

Table 6.6 Some reactions of other group 13 elements (except B)

Reaction	Remark
$4M + 3O_2 \longrightarrow M_2O_3$	• All react at high temperature • All reactions are strongly exothermic • Ga is only superficially oxidised • Tl forms Tl_2O also
$2Al + N_2 \longrightarrow 2AlN$	• Only Al reacts at high temperature

$2M + 3F_2 \longrightarrow 2MF_3$	• All the metals form trihalides
$2M + 3Cl_2 \longrightarrow 2MCl_3$	
$2M + 3Br_2 \longrightarrow 2\,MBr_3$	
$2M + 3I_2 \longrightarrow 2MI_3$	• Al, Ga, In only
$TlI + I_2 \longrightarrow Tl^{\oplus}[I_3]^{\ominus}$	• Thallium(I) triiodide formed
$2M + 6HCl \longrightarrow 2MCl_3 + 3H_2$	• All react with dilute mineral acids. Al is rendered passive by HNO_3 particularly when concentrated
$Al + NaOH + H_2O \longrightarrow NaAlO_2 + H_2$	• Al and Ga only
$Ga + NaOH + H_2O \longrightarrow NaGaO_2 + H_2$	
$2M + 2NH_3 \longrightarrow 2MNH_2 + H_2$	• All metals form amides

6.8 DIAGONAL RELATIONSHIP BETWEEN BORON AND SILICON

Boron, the first member of group 13 elements resemble silicon, the second member of the next group, i.e. group 14. This is a case of diagonal relationship. Boron, in fact, shows more resemblance with silicon than with aluminium. Some points of resemblance of boron and silicon are as follows:

1. **Non-metallic character:** Both boron and silicon are non-metals. Both have high melting points (B = 2453 K, Si = 1693 K), high ionisation enthalpy (B = 801 kJ mol^{-1}, Si = 786 kJ mol^{-1}) and are bad conductors of electricity. However, the conductance increases as the temperature increases. Hence, both behave as semi-conductors at high temperature.
2. **Density and electronegativity:** Both have nearly equal densities (B = 2.35 g cm^{-3}, Si = 2.34 g cm^{-3}) and electronegativities (B = 2.0, Si = 1.8).
3. **Mode of occurrence:** Neither B nor Si occurs free in nature. Both occur in combined state. Both show allotropy.
4. **Tendency to form cations:** Both B and Si do not form cations as their ionisation enthalpies are very high.
5. **Tendency to form covalent compounds:** Both B and Si form compounds which are mostly covalent in nature.
6. **Oxides and oxyacids:** Both B and Si burn in air on heating to form stable oxides, i.e. B_2O_3 and SiO_2 respectively. These oxides are weakly acidic. With water, they form the corresponding weak acids namely boric acid, H_3BO_3, and silicic acid, H_4SiO_4. These oxides on reaction with alkalis form borates and silicates respectively.

$$B_2O_3 + 2NaOH \longrightarrow \underset{\text{Sodium metaborate}}{2NaBO_2} + H_2O$$

or

$$B_2O_3 + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2O$$

$$SiO_2 + 2NaOH \longrightarrow \underset{\text{Sodium metasilicate}}{Na_2SiO_3} + H_2O$$

7. **Reaction with metals:** Both react with metals to form borides and silicides respectively.

$$2B + 3Mg \longrightarrow Mg_3B_2$$

$$Si + 2Mg \longrightarrow Mg_2Si$$

8. **Formation of esters:** Orthoboric acid (H_3BO_3) and ortho-silicic acid (H_4SiO_4) form esters when treated with alcohols in the presence of H_2SO_4, a dehydrating agent.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{H_2SO_4} \underset{\text{Triethylborate}}{(C_2H_5)_3\,BO_3} + 3H_2O$$

The ester formed burns with a green-edged flame. This is used as a qualitative text for borates.

$$H_2SiO_4 + 4C_2H_5OH \xrightarrow{H_2SO_4} \underset{\text{Tetraethylsilicate}}{(C_2H_5)_4\,SiO_4} + 4H_2O$$

9. **Formation of hydrides:** Both B and Si do not combine directly with hydrogen. Hydrides of B and Si are formed in almost identical manner, i.e. by the reduction of their halides with $LiAlH_4$ (lithium aluminium hydride).
10. **Hydrolysis of halides:** Halides of boron and silicon readily gets hydrolysed to give orthoboric acid and orthosilicic acid, respectively.

$$BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF$$

$$SiF_4 + 4H_2O \longrightarrow H_4SiO_4 + 4HF$$

Both BF_3 and SiF_4, if present in excess, dissolve in HF due to the formation of complex halides.

$$BF_3 + HF \longrightarrow H[BF_4]$$

$$SiF_4 + HF \longrightarrow H_2[SiF_6]$$

11. **Reaction with alkali:** Both B and Si react with fused alkalis and evolve hydrogen.

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2\uparrow$$

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2\uparrow$$

12. **Reaction with carbon:** Both B and Si combine with carbon to form carbides, B_4C and SiC, respectively. These are very hard substances and are used for cutting and abrasing purposes.

But apart from the above-mentioned similarities, boron and silicon show certain dissimilarities too, which are as follows:

1. Boron has three electrons in its valence shell ($2s^2\,2p^1$) whereas silicon has four electrons in its valence shell ($3s^2\,3p^2$).
2. Boron is trivalent whereas silicon is tetravalent in its compounds.
3. Boron reacts with nitrogen, N_2, and gives boron nitride (BN), whereas silicon does not react with N_2.

$$2B + N_2 \longrightarrow 2BN$$

4. Boron is oxidised by conc. H_2SO_4 or HNO_3 and give H_3BO_3, whereas silicon does not react.

$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$$

$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$

5. B_2O_3 is amphoteric whereas SiO_2 is acidic in nature.

6.9 ANOMALOUS PROPERTIES OF BORON

Boron, the first member of group 13 elements, shows anomalous behaviour and differs from rest of the members of its family due to the following:

1. Exceptionally small atomic and ionic size
2. High ionisation enthalpy
3. Absence of *d*-orbitals in its valence shell

In many properties boron differs from the other elements of its own group (especially Al) which are as follows:

1. Boron being small in size is harder than rest of the group 13 elements.
2. Boron, due to its small atomic radii, has greater force of attraction between the nucleus and valence shell electrons. Thus B has a very high ionisation enthalpy. This gives boron distinctly non-metallic character, while rest are metals.
3. Boron exhibits maximum covalency of four due to non-availability of *d*-orbitals, in its valence shell while rest of the elements have maximum covalency of six.
4. Boron alone exhibits allotropy.
5. Boron shows +3 oxidation state, while other shows +1 and +3 oxidation states (due to inert pair effect).
6. Boron does not form cation in aqueous solution as the hydration enthalpy is less than the sum total of the first three ionisation enthalpies.
7. Boron forms only covalent compounds while other members of group 13 form both ionic and covalent compounds. For example, BF_3 is covalent, whereas AlF_3 is ionic.
8. Boron does not decompose water or steam while others do.
9. Boron is not attacked by non-oxidising acids, while other elements are attacked.
10. Boron dissolves in conc HNO_3 forming H_3BO_3, while other elements are passive especially Al and Ga.
11. Boron reacts with metals to form borides while other elements do not react and form alloys.
12. The oxide and hydroxide of boron are weakly acidic and dissolve in alkalis forming borates. The oxides of Al and Ga are amphoteric, while those of In and Tl are basic.

$$B_2O_3 + 2NaOH \longrightarrow 2NaBO_2 + H_2O$$

$$B(OH)_3 + NaOH \longrightarrow NaBO_2 + 2H_2O$$

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

$$Al(OH)_3 + HCl \longrightarrow AlCl_3 + 3H_2O$$

(Amphoteric behaviour of Al)

13. The trihalides of group 13 elements being covalent get hydrolysed by water. While boron halides, due to the absence of *d*-orbitals form tetrahedral $[B(OH)_4]^{\ominus}$, rest of the elements, due to the presence of *d*-orbitals form octahedral $[Al(H_2O)_6]^{3+}$ species.
14. The trihalides of B are monomeric while trihalides of other elements of group 13 are dimeric. Due to small size of boron, it cannot accommodate four large-sized halogen atoms around it. The monomeric trihalides, being electron deficient behave as strong Lewis acids and form adducts with ammonia, ethers, etc.

$$F_3B + NH_3 \longrightarrow [F_3B \leftarrow :NH_3]$$

In contrast, the trihalides of other elements of group 13 have halogen-bridged dimeric structure in which a metal completes its octet by accepting an electron pair from a halogen atom of other molecule.

6.10 COMPARISON BETWEEN BORON AND ALUMINIUM

Similarities: As both boron and aluminium have same general electronic configuration, i.e. $ns^2\ np^1$, they have many similarities in their properties.

1. **Electronic configuration:** Both have same number of electrons in their valence shell, i.e. three electrons.
2. **Valency:** Both B and Al are trivalent. They do not show variable valency as their penultimate shells are complete and stable. B^{3+} ion is not known as very high energy ($IE_1 + IE_2 + IE_3$) is required and therefore boron forms covalent compounds. Aluminium also forms covalent compounds. It can, however, form ionic compound with strong electron accepting atoms or groups. Due to small size and high charge on Al^{3+}, it has high polarising power. This gives rise to covalent character even in ionic compounds, e.g. $AlCl_3$, $AlBr_3$ and AlI_3 have covalent character.
3. **Oxidation state:** In most of their compounds, both show common oxidation state of +3. Boron, however, also shows an oxidation state of –3 in the metal borides.

Compound	Oxidation state of B/Al
B_2O_3 (Boric anhydride)	+3
BCl_3 (Boron trichloride)	+3
H_3BO_3 (Orthoboric acid)	+3
Al_2O_3 (Aluminium trioxide)	+3
$AlCl_3$ (Aluminium trichloride)	+3
$Al(OH)_3$ (Aluminium hydroxide)	+3
Mg_3B_2 (Magnesium boride)	–3

4. **Reaction with conc H_2SO_4:** Both react with conc H_2SO_4 to evolve SO_2.

$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + SO_2\uparrow$$

$$2Al + 6H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3SO_2\uparrow$$

5. **Reaction with alkalis:** Both dissolve in alkali and evolve H_2.
$2B + 6\,NaOH \longrightarrow 2Na_3BO_3 + 3H_2$
$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$
6. **Formation of oxides:** Both form oxides when heated with oxygen at high temperature.
$4B + 3O_2 \xrightarrow{700°C} 2B_2O_3$
$4Al + 4O_2 \xrightarrow{800°C} 2Al_2O_3$
7. **Amphoteric oxides:** Their oxides are amphoteric, i.e. dissolve in acids as well as bases to form salts.
$B_2O_3 + 6HCl \longrightarrow 2BCl_3 + 3H_2O$
$B_2O_3 + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2O$
$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$
$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$
8. **Formation of nitrides:** Both when heated with nitrogen or ammonia form nitrides, MN.
$2B + N_2 \longrightarrow 2BN;\quad 2B + 2NH_3 \longrightarrow 2BN + 3H_2$
$2Al + N_2 \longrightarrow 2AlN;\ 2Al + 2NH_3 \longrightarrow 2AlN + 3H_2$
9. **Formation of sulphides:** Both when heated with sulphur at high temperature form sulphides, M_2S_3.
$2B + 3S \longrightarrow B_2S_3$
$2Al + 3S \longrightarrow Al_2S_3$

These sulphides are hydrolysed by water.
$B_2S_3 + 6H_2O \longrightarrow 2H_3BO_3 + 3H_2S$
$Al_2S_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2S$
10. **Formation of chlorides:** Both form trichlorides by direct combination with Cl_2 or by passing Cl_2 over heated mixture of their oxides and charcoal.
$2B + 3Cl_2 \longrightarrow 2BCl_3$
$B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO$
$2Al + 3Cl_2 \longrightarrow 2AlCl_3$
$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO$
11. **Formation of alkyl compounds:** Both form similar type of alkyl compounds.
$2BCl_3 + 3Zn(CH_3)_2 \longrightarrow 2B(CH_3)_3 + 3Zn\,Cl_2$
$2Al + 3Hg(CH_3)_2 \longrightarrow 2Al(CH_3)_3 + 3Hg$
12. **Reducing agents:** Both behave as strong reducing agents.
$4B + 3CO_2 \longrightarrow 2B_2O_3 + 3C$
$4Al + 3CO_2 \longrightarrow 2Al_2O_3 + 3C$
$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$
13. **Action of steam:** Boron reacts with steam at red heat liberating hydrogen.
$2B + 3H_2O \longrightarrow B_2O_3 + 3H_2$
Aluminium decomposes boiling water.
$2Al + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2$

Dissimilarities: Due to difference in size and ionisation enthalpy of B and Al, they show many different properties as given below.

Boron	Aluminium
1. There are two electrons in the penultimate shell. ($1s^2\,2s^2\,2p^1$)	1. There are eight electrons in the penultimate shell. ($1s^2\,2s^2\,2p^6\,3s^2\,3p^1$)
2. Boron is a non-metal.	2. Aluminium is a metal.
3. It is a bad conductor of heat and electricity.	3. It is a good conductor of heat and electricity.
4. It shows allotropy. The allotropic modifications are crystalline and amorphous.	4. It does not show allotropy.
5. Its crystalline form is very hard.	5. It is sufficiently soft.
6. It forms only covalent compounds.	6. It forms both covalent and electrovalent compounds.
7. It reacts with hydrogen to form number of stable hydrides.	7. It does not form any stable hydride.
8. It does not react with dilute acids.	8. It reacts with dilute acids and evolve H_2. $2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2\uparrow$
9. It gets oxidised by conc HNO_3 to form $B(OH)_3$. $B + 3HNO_3 \longrightarrow H_3BO_3 + 2NO_2$	9. It becomes passive with conc H_2SO_4 due to the formation of a layer of Al_2O_3 on its surface which makes the metal inert.
10. Its maximum covalency is 4.	10. Its maximum covalency is 6.
11. It dissolves in fused alkalis to evolve H_2. $2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$	11. It dissolves in hot alkalis to evolve H_2. $2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$
12. Borates are very stable.	12. Aluminates are less stable.
13. $B(OH)_3$ is weakly acidic.	13. $Al(OH)_3$ is amphoteric.
14. BCl_3 is a fuming liquid.	14. $AlCl_3$ is a solid.
15. It combines with metals to form borides.	15. It combines with metals to form alloys.

ILLUSTRATION 6.1

a. Standard electrode potential value E° for Al^{3+}/Al is -1.66 V and that of Tl^{3+}/Tl is $+1.26$ V. Predict about the formation of M^{3+} ion in solution and compare the electropositive character of the two metals.

b. White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

c. Boron is unable to form BF_6^{3-} ion. Explain.

Sol.

a. Standard electrode potential values for two half- cell reactions suggest that aluminium has high tendency to form $Al^{3+}_{(aq)}$ ions, whereas Tl^{3+} is not unstable in solution but is a powerful oxidising agent also. Thus Tl^{+} is more stable in solution than Tl^{3+}. Aluminium being able to form +3 ions easily, is more electropositive than thallium.

b. Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate HCl gas. Moist HCl appears white in colour.

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$$

c. Due to non-availability of *d*-oribtals, boron is unable to expand its octet. Therefore, the maximum covalency of boron cannot exceed 4.

ILLUSTRATION 6.2

Explain the following:

a. Boron has high melting and boiling points.

b. The $p\pi$–$p\pi$ back bonding occurs in the halides of boron and not in those of aluminium.

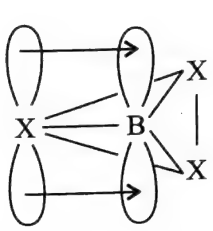
c. Boron and aluminium halides behave as Lewis acids.

d. Aluminium forms $[AlF_6]^{3-}$ ion, but boron does not form $[BF_6]^{3-}$ ion.

Sol.

a. Boron has giant covalent polymeric structure both in solid and liquid states, thus it has high melting and boiling points.

b. The formation of $p\pi$–$p\pi$ back bonding involves donation of an electron pair from the filled orbital of the atom forming a 'σ' bond with the central atom. The tendency to show back bonding depends on the size of the atoms involved. This tendency decreases as the size of the central atom increases. Since boron has smaller size as compared to aluminium, back bonding is more feasible in boron halides as compared to aluminium.



c. Both boron and aluminium in their halides possess six electrons in their valence shell. Because these are short of two electrons to complete their octet and thus behave as electron-deficient compounds. They can easily accept a pair of electron from a donor ion/molecule and thus behave as Lewis acid.

d. Due to the absence of low-lying vacant *d*-orbitals in boron, it cannot expand its coordination number beyond four and thus boron does not form $[BF_6]^{3-}$ ion. On the other hand, aluminium due to the presence of vacant *d*-orbitals in valence shell can expand its coordination number beyond 4 (up to 6) and thus easily form $[AlF_6]^{3-}$ ion.

ILLUSTRATION 6.3

The first ionisation enthalpy of group 13 elements are:

Element	Boron	Aluminium	Gallium	Indium	Thallium
Symbol	B	Al	Ga	In	Tl
IE_1 ($kJmol^{-1}$)	801	577	579	558	589

Explain this deviation from the general trend.

Sol. Down the group (↓), from B to Al, the ionisation enthalpy decreases due to increase in size and screening effect. Ionisation enthalpy of Ga is slightly higher than Al, Ga and In. These deviations from the general trend can be explained on the basis of electronic configuration.

Element	B	Al	Ga	In	Tl
Electronic configuration	$[He]2s^2\ 2p^1$	$[Ne]3s^2\ 3p^1$	$[Ar]3d^{10}\ 4s^2\ 4p^1$	$[Kr]\ 4d^{10}\ 5s^2\ 5p^1$	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$

B and Al have noble gas core beneath the valence shell electrons, but at Ga, there is inclusion of lesser shielding fully filled 3*d* orbital in between the noble gas core and the valence shell electrons, which results in increase in effective nuclear charge and valence shell electrons are tightly held by the nucleus and hence higher energy is required for their removal. Hence, there is an increase in ionisation enthalpy from Al to Ga. At Tl, fully filled lesser shielding 4*f* as well as 5*d* orbitals are present which result in much higher effective nuclear charge at Tl. Hence, IE_1 is much higher than Al, Ga and In.

ILLUSTRATION 6.4

Answer the following:

a. Name the element of group 13 which forms the most stable compound in +1 oxidation state.

b. Name the element of group 13 which has the highest first ionisation enthalpy.

c. Name the element of group 13 which is used as a reducing agent in metallurgical processes.

d. Name the element of group 13 which can show covalency maximum of four only.

e. Name the compound of aluminium which is used as a germicide and coagulant in the purification of water.

f. Name the first two elements of group 13.

Sol.

a. Thallium b. Boron
c. Aluminium d. Boron
e. Potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
f. Boron and aluminium

ILLUSTRATION 6.5

Give reasons for the following:

a. No visible reaction occurs when aluminium is left in contact with conc HNO_3.
b. The hydroxides of Al and Fe are insoluble in water. However, NaOH is used to distinguish one from another.
c. Anhydrous $AlCl_3$ cannot be prepared by heating hydrated aluminium chloride.
d. Aluminium vessels should not be cleaned with cleansing agent containing washing soda.
e. Duralumin is used in aircraft industry.

Sol.

a. Aluminium is rendered passive by conc HNO_3 due to the formation of a layer of oxide (Al_2O_3) on the surface.
b. Aluminium hydroxide, $Al(OH)_3$, dissolves in NaOH, whereas ferric hydroxide, $Fe(OH)_3$, is insoluble in NaOH.

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$
$$Fe(OH)_3 + NaOH \not\longrightarrow \text{No reaction}$$

c. Anhydrous $AlCl_3$ cannot be prepared by heating hydrated $AlCl_3$, as on heating, $AlCl_3 \cdot 6H_2O$ gets hydrolysed to form Al_2O_3.

$$2\,AlCl_3 \cdot 6H_2O \longrightarrow 2Al(OH)_3 + 6HCl$$
$$2\,Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

d. Aluminium vessels should not be cleaned with cleaning agent containing washing soda as Na_2CO_3 undergoes hydrolysis to give NaOH and Al dissolves in NaOH.

$$Na_2CO_3 + 2H_2O \longrightarrow 2NaOH + CO_2 + H_2O$$
$$2H_2O + 2Al + 2NaOH \longrightarrow 2NaAlO_2 + 3H_2$$

e. Duralumin is an alloy of aluminium whose composition is 95% Al, 4% Cu, 0.5% Mg and 0.5% Mn. It is light and tough. It has resistant to corrosion and thus is used in aircraft industry.

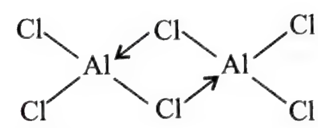
ILLUSTRATION 6.6

Explain the following:

a. Aluminium vessels can be used to store conc HNO_3.
b. $AlCl_3$ forms a dimer, but BCl_3 does not.
c. Al metal is frequently used as a reducing agent for the extraction of metal such as Cr, etc.
d. Al cannot be prepared by the electrolysis of aqueous solution of its salt.
e. The B–X distance is shorter than what is expected theoretically in BX_3 molecule (X = F, Cl, Br, I).
f. Although the ionisation potential of B (8.30 eV) is less than gold (9.22 eV), yet B is a non-metal while gold is a metal.

Sol.

a. Aluminium metal is rendered passive by nitric acid (HNO_3) due to the formation of an oxide layer (Al_2O_3) on its surface. Hence, Al vessel is not attacked by conc HNO_3 and conc HNO_3 can be easily stored in aluminium vessel.
b. Both BCl_3 and $AlCl_3$ are electron-deficient compounds as both B and Al have only six electrons around them in BCl_3 and $AlCl_3$, respectively and hence their octet is incomplete. To complete their octet, $p\pi$–$p\pi$ back bonding is not possible in $AlCl_3$ due to increase in size of Al. Hence, Al completes its octet by forming dimer in which Cl atom of one $AlCl_3$, donates an electron pair in the vacant $3p$ orbital of Al by forming a coordinate bond, whereas in BCl_3, $p\pi$–$p\pi$ back bonding occurs and BCl_3 eixsts as a monomer and not as a dimer.



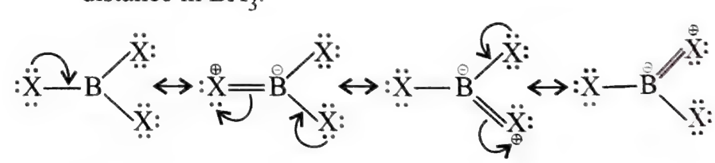
c. Aluminium has great affinity for oxygen. Aluminium thus removes oxygen from the oxides of less electropositive metals and as a good reducing agent.

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$$

d. Aluminium cannot be prepared by the electrolysis of aqueous solution of its salt, as discharge potential of aluminium is higher than the discharge potential of hydrogen. Thus, the aqueous solution containing Al^{3+} ions and $H^{\oplus}$ ions, when electrolysed, the $H^{\oplus}$ ions rather than Al^{3+} ions are discharged at cathode and hydrogen is liberated.

At cathode: $2H^{\oplus} + 2e^{\ominus} \longrightarrow H_2\uparrow$

e. Due to $p\pi$–$p\pi$ back bonding in BX_3, the molecule has double bond character, which results in shortening of B–X bond distance in BX_3.



f. Despite the fact that ionsation potential of boron (8.30 eV) is less than gold (9.22 eV), boron is a non-metal. This is due to difference in structure in the solid state. In general, metals have large number of atoms as neighbours as compared to non-metal. Gold has 12 atoms as neighbours, whereas boron has 6 or less atoms as neighbours in the solid state.

ILLUSTRATION 6.7

a. What are the special features of structure of boron?
b. Which alloy of aluminium is used in air-craft industry?
c. When finely powdered Al is suddenly exposed to air, it catches fire. Why?
d. Write a balanced equation for the preparation of elemental boron by reduction of BBr_3 with dihydrogen.

a. Boron is a symmetrical solid with icosahedral shape. There are 20 faces (equilateral triangle). The faces meet as 12 corners. Each icosahedran consists of 12 boron atoms, 6 of them are bonded by a three-centre two-electron (3c, 2e) bond (2.02 Å) in separated icosahedra.

b. An alloy of aluminium which is used in air-craft industry is duralumin. Its composition is 95% Al, 4%, Cu, 0.5% Mn and 0.5% Mg.

c. Finely powdered aluminium, when suddenly exposed to air, reacts vigorously with aerial oxygen, O_2. The reaction is highly exothermic and therefore Al catches fire.

$$4Al_{(s)} + 3O_{2(g)} \longrightarrow 2Al_2O_{3(s)} \quad \Delta H = -310 \text{ kJ mol}^{-1}$$

d. $2BBr_{3(g)} + 3H_{2(g)} \longrightarrow 2B_{(s)} + 6HBr_{(g)}$

ILLUSTRATION 6.8

In a regular B_{12} icosahedran:

a. How many boron atoms are equidistant from a given boron atom?

b. How many edges are there?

c. How many valence electrons are there?

d. Can each edge line represent an electron pair bond?

e. Explain the type of bonding involved in elemental boron?

Sol. In a regular B_{12} icosahedran:

a. Five boron atoms are equidistant from a given boron atom.

b. There are 30 edges, i.e. 5 from the top B-atom, 5 around the upper pentagon, 10 from the upper pentagon to the low, 5 around the lower pentagon and 5 to the bottom boron atom.

c. Valence shell electronic configuration of B is $2s^2\ 2p^1$, so each boron atom has 3 valence electrons. Total number of valence electrons in B_{12} icosahedra $= 3 \times 12 = 36$ electrons.

d. No, there are 30 edges in B_{12} icosahedra, so the total electron should be $30 \times 2 = 60$ electrons. Since there are not 60 electrons, hence each edge line cannot represent an electron pair.

e. There must be some (3c, 2e) bridge bonding, just as in diborane.

ILLUSTRATION 6.9

Predict whether $Tl^{\oplus}$ will disproportionate in aqueous solution:

$$Tl^{3+} \xrightarrow{1.25\text{ V}} Tl^{\oplus} \xrightarrow{-0.34\text{ V}} Tl$$

Sol. Disproportionation of $Tl^{\oplus}$ can be represented as:

$Tl^{\oplus} \longrightarrow Tl^{3\oplus} + Tl \qquad E^{\ominus} = ? \qquad$ ...(i)

Given, $2e^{\ominus} + Tl^{3+} \longrightarrow Tl^{\oplus} \qquad E^{\ominus} = +1.25$ V ...(ii)

$e^{\ominus} + Tl^{\oplus} \longrightarrow Tl \qquad E^{\ominus} = -0.34$ V ...(iii)

Eq. (iii) × (ii) $\Rightarrow 2\,Tl^{\oplus} + 2e^{\ominus} \longrightarrow 2Tl \quad E^{\ominus} = 0.34$ V ...(iv)

Reverse Eq. (ii) $\Rightarrow Tl^{\oplus} \longrightarrow Tl^{3+} + 2e^{\ominus} \quad E^{\ominus} = 1.25$ V ...(v)

Add Eqs. (iv) + (v) $\Rightarrow \overline{3Tl^{\oplus} \longrightarrow 2\,Tl + Tl^{3+} \quad E^{\ominus} = -1.59 \text{ V}}$

Because $E^{\ominus}$ value is highly negative, $Tl^{\oplus}$ will have no tendency for disproportionation.

ILLUSTRATION 6.10

a. Al is a good reducing agent. Explain.

b. A metallic element, M, forms two stable chlorides with formula MCl and MCl_3 respectively. Where the element M is to be placed in the periodic table?

Sol.

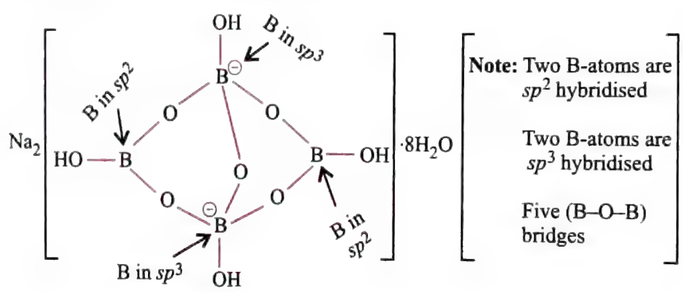
a. Reducing agent can easily lose electron and get oxidised since Al has low ionisation enthalpy and has + ve reduction potential, it acts as good reducing agent.

b. Metal, M, forms chlorides—MCl and MCl_3. The oxidation state of M in MCl is +1 and in MCl_3 is +3. This implies that metal M has three electrons in its valence shell and M belongs to group 13, i.e. boron family.

6.11 SOME IMPORTANT COMPOUNDS OF BORON AND ALUMINIUM

6.11.1 Borax ($Na_2B_4O_7 \cdot 10H_2O$ or $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$)

Borax or sodium tetraborate contains the tetranuclear units $[B_4O_5(OH)_4]^{2-}$ and therefore it is correctly formulated as $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ (Fig. 6.10).



sp^2 hybridised B-atoms only participate in ($p\pi$-$p\pi$) back bonding.

Fig. 6.10 Structure of $Na_2[B_4O_5(OH)_4].8H_2O$

Preparation:

1. **From tincal:** Naturally occurring crude form of borax is known as TINCAL and contains ~ 55% of borax and is found in dried lakes of Tibet, Sri Lanka and California. Tincal is dissolved in water, filtered, concentrated and crystallised when pure borax is obtained.

2. **From colemanite:** Finely powered colemanite, $Ca_2B_6O_{11}$, is boiled with concentrated solution of sodium carbonate.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \xrightarrow[\text{Boil}]{\Delta} 2CaCO_3\downarrow + \underset{\text{Borax}}{Na_2B_4O_7} + \underset{\text{Sodium metaborate}}{2NaBO_3}$$

On filtration, $CaCO_3$ precipitate is removed. On concentration of the filtrate, white crystals of borax separates out. $NaBO_3$ is converted into borax, by passing a current of CO_2 through the mother-liquor.

$$4NaBO_3 + CO_2 \longrightarrow Na_2CO_3 + Na_2B_4O_7$$

3. **From boric acid:** By neutralising boric acid by sodium carbonate.

$$4B(OH)_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + CO_2 + 6H_2O$$

Properties:

1. **Forms of borax:** Borax is known in three forms.

a. Prismatic borax ($Na_2B_4O_7 \cdot 10H_2O$)	• It is the common form of borax and is the decahydrate form. • It is obtained by crystallising the solution at ordinary temperature. • It is white crystalline solid. • It is fairly soluble in cold water but freely soluble in hot water.
b. Octahedral borax ($Na_2B_4O_7 \cdot 5H_2O$)	• It is in pentahydrate form. • It is obtained by crystallising solution at 60°C. • It is also known as jeweller's borax.
c. Borax glass ($Na_2B_4O_7$)	• It is anhydrous form. • It is obtained by heating the common form above its melting point. • It is colourless glassy mass. • It is not stable in moist air as it absorbs moisture readily and gradually convert into decahydrate form.

2. **Basic nature:** Aqueous solution of borax is alkaline due to its hydrolsis.

$$Na_2B_4O_7 + H_2O \rightleftharpoons \underset{\text{Strong base}}{2NaOH} + \underset{\text{Weak acid}}{4H_3BO_3}$$

Borax is therefore used as a water softener and cleaning agent.

3. **Action of heat:** On heating, initially borax swells up due to loss of its water of crystallisation. On further heating, it melts to give a clear liquid, which solidifies into transparent glass like bead known as *borax bead*. Borax bead comprises sodium metaborate ($NaBO_2$) and boric anhydride (B_2O_3).

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \xrightarrow{\Delta} \underbrace{\underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}}_{\text{Borax bead}}$$

Borax bead is employed in the qualitative test for the detection of some coloured basic radicals, i.e. copper (Cu), iron (Fe), chromium (Cr), manganese (Mn), cobalt (Co) and nickel (Ni).

4. Aqueous solution of borax behaves as a buffer because it consists of weak acid and its salt with strong base.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 2Na[B(OH)_4] + 2H_3BO_3$$

5. **Reaction with NaOH:**

$$Na_2B_4O_7 + 2NaOH \longrightarrow \underset{\text{Sodium metaborate}}{4NaBO_2} + H_2O$$

6. **Reaction with H_2SO_4:** On adding hot and conc H_2SO_4 to hot and conc solution of borax, boric acid is formed.

$$Na_2B_4O_7 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2B_4O_7$$
$$H_2B_4O_7 + 5H_2O \longrightarrow 4H_3BO_3$$
$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

7. **Reaction with ethyl alcohol and H_2SO_4:** On heating borax with ethyl alcohol and conc H_2SO_4, vapours of triethylborate ($B(OC_2H_5)_3$) are produced, which burn giving a green-edged flame.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

$$H_3BO_3 + 3C_2H_5OH \longrightarrow B(OC_2H_5)_3 + 3H_2O$$

This reaction is used for qualitative analysis of borax or borate ion.

Uses:

1. As a flux in soldering.
2. In the manufacture of heat resistant borosilicate glass (pyrex).
3. In the manufacture of enamels and glass for earthen wares, i.e. pottery etc. The glazed surface is resistant to heat, stains and scratches.
4. To make sodium peroxoborate, $\{Na_2[(OH)_2B(O\text{–}O)_2B(OH)_2] \cdot 6H_2O\}$ as follows:

Step i: Strongly heating borax to produce sodium metaborate, $NaBO_2$.

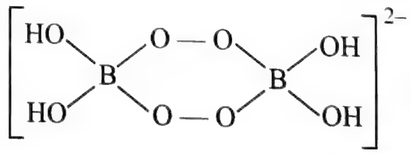
$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \xrightarrow{\Delta} NaBO_2 + B_2O_3$$

Step ii: Oxidising $NaBO_2$ formed in step (i), with H_2O_2.

$$2NaBO_2 + 2H_2O_2 + 6H_2O \longrightarrow \underset{\text{Sodium peroxoborate}}{Na_2[(OH)_2B(O-O)_2B(OH)_2].6H_2O}$$

Sodium peroxoborate is used as a brightner (as it absorbs UV light and emit visible light) in washing powders. It is compatible with enzymes which are added to some 'biological' powders. In very hot water, the peroxide linkages O–O break down to give H_2O_2.



Peroxoborate ion

That is why it also acts as a bleaching agent.

5. In water softening.
6. For borax bead test.
7. As a stiffening agent for candle wicks.
8. In leather industry, for cleaning skins.
9. For impregnating match-sticks to prevent after glow.

6.11.2 Boric Acid or Oxyacids of Boron

Several boric acids are known, e.g.

Orthoboric acid	H_3BO_3 or $B(OH)_3$
Metaboric acid	HBO_2

...yroboric acid	$H_6B_4O_9$ or $2B_2O_3 \cdot 3H_2O$
...traboric acid	$H_2B_4O_7$ or $B_2O_3 \cdot H_2O$

Out of these, orthoboric acid is generally referred to as boric acid and is most important as it is stable both in the solid and solution state. The remaining acids are stable in the solid state and gradually change into orthoboric acid in solution.

6.11.3 ORTHOBORIC ACID (H_3BO_3) OR $B(OH)_3$

Preparation:

1. **By hydrolysis of boron compounds:** Orthoboric acid can be prepared by hydrolysis of any trivalent boron compound such as boron halides, hydrides, nitride etc.

$BX_3 + 3H_2O \longrightarrow B(OH)_3 + 3HX$ (where X = F, Cl, Br)

$B_2H_6 + H_2O \longrightarrow 2B(OH)_3 + 6H_2$

$BN + 3H_2O \longrightarrow B(OH)_3 + NH_3$

2. **From borax:** Hot and concentrated solution of borax is mixed with concentrated HCl or H_2SO_4. The two on reaction gives boric acid. The resulting solution is cooled, which results in the separation of white crystalline boric acid.

$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$

Or $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$

3. **From colemanite:** Finely powdered colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$ is dissolved in boiling water and SO_2 is passed through the solution, which results in the formation of boric acid and calcium bisulphite. The resulting solution remains in the solution, while boric acid crystallises out.

$Ca_2B_6O_{11} + 4H_2O + 4SO_2 \longrightarrow 2Ca(HSO_3)_2 + H_4B_6O_{11}$

$H_4B_6O_{11} + 7H_2O \longrightarrow 6H_3BO_3$

$Ca_2B_6O_{11} + 4SO_2 + 11H_2O \longrightarrow 2Ca\,(HSO_3)_2 + 6H_3BO_3$

Properties:

1. Boric acid is white crystalline solid which is flaky, soft and soapy to touch (explained on the basis of its structure).
2. It is slightly soluble in cold water, more soluble in hot water and volatile in steam.
3. Boric acid acts as weak monobasic acid.

$B(OH)_3 + H_2O \rightleftharpoons [B(OH)_4]^{\ominus} + H_3O^{\oplus}$ $(pK_a = 9.25)$

Since $B(OH)_3$ reacts only partially with water to form $H_3O^{\oplus}$ and $[B(OH)_4]^{\ominus}$, it behaves as a weak acid. Moreover, $B(OH)_3$ is accepting one $\overset{\ominus}{O}H$ group, from H_2O, hence it is monobasic in nature.

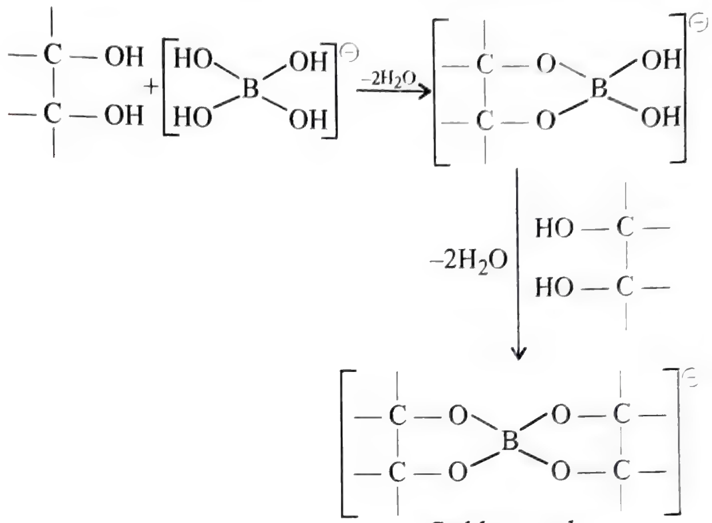
4. Boric acid acts not as a protonic acid, but as a Lewis acid. As evident from the above reaction, $B(OH)_3$ does not donate a proton ($H^{\oplus}$), hence does not act as protonic acid, but it accepts a pair of electron from $\overset{\ominus}{O}H$ ion of solvent (water) molecule, hence behaves as Lewis acid.
5. Boric acid behaves as a strong acid in presence of *cis*-diols. Since $B(OH)_3$ behaves as a weak acid, it cannot be titrated satisfactorily with NaOH, as a sharp end point is not obtained. If certain organic polyhydroxy compound containing *cis*-diol group such as glycerol, mannitol or sugars are added to the titration mixture, then $B(OH)_3$ behaves as a strong

monobasic acid. It can now be titrated with NaOH and the end point is detected using phenolphthalein as an indicator (indicator changes colour in the pH range 8.3–10.0).

$B(OH)_3 + NaOH \rightleftharpoons Na[B(OH)_4]$

or $NaBO_2 + 2H_2O$
Sodium metaborate

The reason being, *cis*-diol compound when added in the reaction mixture enhances the acidic property of $B(OH)_3$,



Stable complex

as it forms very stable complex with $[B(OH)_4]^{\ominus}$ (formed in the above reaction), thus effectively removing it from the solution. Removal of one of the products on the right-hand side of the equation disturbs the equilibrium and the reaction proceeds completely to the right. Thus, all the $[B(OH)_4]^{\ominus}$ reacts with NaOH, or in other words, $B(OH)_3$ behaves as a strong acid in the presence of *cis*-diols.

6. Action of heat:

$H_3BO_3 \xrightarrow[-H_2O]{473\,K} \underset{\text{Metaboric acid}}{HBO_2} \xrightarrow{\text{Red heat}} \underset{\text{Boron oxide (also known as boric anhydride)}}{B_2O_3}$

$B(OH)_3 \xrightarrow{473\,K} \underset{\text{Metaboric acid}}{HBO_2} + H_2O$

$4HBO_2 \xrightarrow{410\,K} \underset{\text{Tetraboric acid}}{H_2B_4O_7} + H_2O$

$H_2B_4O_7 \xrightarrow{\text{Red heat}} 2B_2O_3 + H_2O$

7. With C_2H_5OH: In the presence of dehydrating agents like conc H_2SO_4, $B(OH)_3$ reacts with ethanol to give triethylborate, which burns with a green-edged flame.

$B(OH)_3 + 3C_2H_5OH \xrightarrow[\text{Heat}]{H_2SO_4} B(OC_2H_5)_3 + 3H_2O$

This reaction is used in the qualitative test of boric acid or borates in the mixture analysis.

8. With CaF_2 and conc H_2SO_4:

$2B(OH)_3 + 3H_2SO_4 + 3CaF_2 \xrightarrow{\Delta} 3CaSO_4 + 2BF_3\uparrow + 6H_2O$

BF_3 burns with a green-edged flame. This reaction is used in the qualitative test of boric acid or borates in the mixture analysis.

9. With soda ash:

$$\underset{\text{Soda ash}}{4B(OH)_3 + Na_2CO_3} \longrightarrow \underset{\text{Borax}}{Na_2B_4O_7} + 6H_2O + CO_2$$

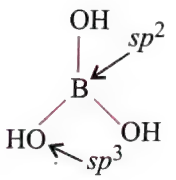
6.11.4 Structure and Bonding of Orthoboric Acid

Orthoboric acid contains triangular borate, BO_3^{3-} unit in which B is sp^2 hybridised.

In the solid state, $B(OH)_3$ units are hydrogen bonded together into two-dimensional sheets with almost hexagonal symmetry. The layers are quite a large distance apart (3.18 Å) and thus the crystal breaks quite easily into fine particles.

It may be seen from Fig. 6.11, that each B-atom of each BO_3^{3-} unit remains bonded to three oxygen atoms and each O-atom is bonded to one H by covalent bond and other H by hydrogen bond. Thus H-atom acts as a bridge between the two O-atoms of different BO_3^{3-} units.

Note: In H_3BO_3, states of hybridisation of B and O are sp^2 and sp^3 respectively as shown below:



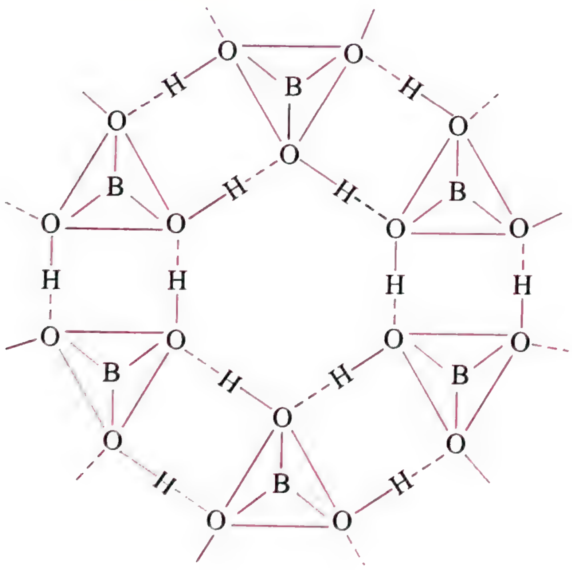


Fig. 6.11 Structure of boric acid [(---) Hydrogen bond, (—) covalent bond]

6.11.5 Boron Hydrides

The binary compounds of boron and hydrogen are known as *boron hydrides* or *boranes* (by analogy with alkanes). None of group 13 elements reacts directly with hydrogen, but many hydrides are known. The simplest boron hydride known is diborane, B_2H_6.

Classification of boranes: All the known boranes can be classified into two series.

1. B_nH_{n+4} series

These are also known as **nidoboranes**

B_2H_6 diborane(6) or diborane

B_5H_9 pentaborane(9)

B_6H_{10} hexaborane(10)

B_8H_{12} octaborane(12)

$B_{10}H_{14}$ decaborane(14)

2. B_nH_{n+6} series

These are also known as **arachnoboranes**

B_4H_{10} tetraborane(10)

B_5H_{11} pentaborane(11)

B_6H_{12} hexaborane(12)

B_8H_{14} octaborane(14)

B_9H_{15} enneaborane(15) or nonaborane(15)

The boranes are named as follows:

1. The latin prefix (di, tri, tetra etc.) is used before 'borane' to indicate the number of boron atoms in compound.
2. Immediately following the '*e*' in borane, the number of hydrogen atoms are written in parenthesis using arabic numerals.

   e.g. B_5H_{11} is pentaborane(11)

The borones were originally prepared by the hydrolysis of magnesium boride by hydrochloric acid (Stock's method).

$$B_2O_3 + 3Mg \xrightarrow{\Delta} 2B + 3MgO$$

$$2B + 3Mg \longrightarrow Mg_3B_2 \text{ (Magnesium boride)}$$

$$Mg_3B_2 + HCl \longrightarrow \text{Mixture of boranes} + H$$

Mixture of boranes may be separated by liquefying the gaseous mixture (by passing though a vessel immersed in liquid air) and then fractionating the liquid obtained. This method has now been superseeded except for making B_4H_{10}. Boranes are now prepared using diborane.

6.11.6 Diborane (B_2H_6)

Preparation:

1. By the reaction of BCl_3 with hydrogen over a Cu–Al catalyst at 450°C.

$$2BCl_3 + 6H_2 \xrightarrow[450°C]{Cu-Al} B_2H_6 + 6HCl$$

2. By reduction of $BF_3{\cdot}O(C_2H_5)_2$ (boron trifluoride ether complex) with $LiAlH_4$ in ether:

(i) $$4BF_3{\cdot}O(C_2H_5)_2 + 3LiAlH_4 \xrightarrow[\text{Reflux}]{\text{Ether}} 2B_2H_6 + 3Li[AlF_4] + 4(C_2H_5)_2O$$

(ii) $$LiBH_4 + 2FeCl_3 \xrightarrow[\text{Ether}]{195\text{ K}} 2FeCl_2 + 2LiCl + H_2 + B_2H_6$$

$$2LiBH_4 + FeCl_2 \xrightarrow[\text{Ether}]{273\text{ K}} Fe + 2LiCl + H_2 + B_2H_6$$

$$4LiBH_4 + SiCl_4 \longrightarrow SiH_4 + 4LiCl + 2B_2H_6$$

(iii) Alkali metal borohydrides are handy source of diborane.

$$2NaBH_4 + 2HCl \longrightarrow 2NaCl + 2H_2 + B_2H_6$$

$$2NaBH_4 + 4BF_3 \longrightarrow 3NaBF_4 + 2B_2H_6$$

3. **Lab method:** By the oxidation of sodium borohydride ($NaBH_4$) by iodine (I_2) in the solvent diglyme (diglyme is a polyether, $CH_3OCH_2CH_2OCH_2CH_2OCH_3$, i.e. diethylene glycol dimethyl ether)

4. **Industrial method of preparation:** By the reduction of BF_3 with NaH, $LiAlH_4$ and $NaBH_4$.

(i) $2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$

(ii) $4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3$

(iii) Oxidation of $NaBH_4$ with I_2

$$2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$$

5. By the reaction of sulphuric acid with $NaBH_4$.

$$2NaBF_4 + H_2SO_4 \longrightarrow B_2H_6 + 2H_2 + Na_2SO_4$$

6. By reducing BF_3 with $NaBH_4$ in ether.

$$4BF_3{\cdot}O(C_2H_5)_2 + 3NaBH_4 \longrightarrow 2B_2H_6 + 2NaBH_4 + 4(C_2H_5)_2O$$

This method is particularly used when diborane is required as an intermediate. It is produced in situ and used without the need to isolate or purify it.

Properties:

1. **Colourless:** Diborane is a colourless gas, with melting point of –165°C and boiling point of –92.5°C.

2. **Highly reactive:** It is a highly reactive gas and must be handled with care. It catches fire spontaneously in air and the reaction is explosive in nature as a large amount of heat is produced.

$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O \quad \Delta_fH^{\ominus} = -2165\ \text{kJ mol}^{-1}$

In laboratary, diborane is handled in vacuum frame, since it react with grease used to lubricate taps, special taps must be used.

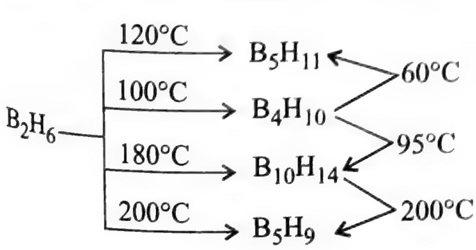
3. **Reaction with water:** B_2H_6 is instantaneously hydrolysed by H_2O to form boric acid.

$B_2H_6 + 6H_2O \longrightarrow 2B(OH)_3 + 6H_2\uparrow$

4. **Reaction with alkalis:** Diborane dissolves in strong alkalis (NaOH or KOH) to produce metaborates and hydrogen gas.

$B_2H_6 + 2NaOH + 2H_2O \longrightarrow \underset{\text{Sodium metaborate}}{2NaBO_2} + 6H_2$

5. **Action of heat:** On heating diborane alone or with hydrogen, higher boranes are synthesised or diborane polymerises to higher boranes on heating to 100–250°C.



At red heat, boranes decompose to boron and hydrogen.

6. **Reaction with amines:** Diborane being an electron-deficient compound accepts electron pairs from Lewis bases and behaves as Lewis acid. B_2H_6 undergoes cleavage with amines forming simple adducts.

$B_2H_6 + 2\,Me_3N \longrightarrow 2\,[Me_3N \longrightarrow BH_3]$

7. **Reaction with ammonia:** Diborane reacts with ammonia, a Lewis base, but the products formed depend on conditions. B_2H_6 reacts with excess of NH_3 (at –120°C) to form an additional product, $B_2H_6{\cdot}2NH_3$ (diammoniate of diborane), which has been found to be an ionic compound, comprising $[H_3N \longrightarrow BH_2 \longleftarrow NH_3]^{\oplus}$ and $[BH_4]^{\ominus}$ ions. On heating at 200°C, it forms borazine.

$$B_2H_6 + 2NH_3 \xrightarrow[\text{Excess } NH_3]{\text{Low temp }(-120°C)} [H_2B\,(NH_3)_2]^{\oplus}\,[BH_4]^{-}$$

$$B_2H_6 + NH_3 \xrightarrow[\text{Excess } NH_3]{\text{High temp}} \underset{\text{Boron nitride}}{(BN)_x}$$

$$3B_2H_6 + 3NH_3 \xrightarrow[1B_2H_6:2NH_3]{200°C} \underset{\text{Borazine or borazole}}{2B_3N_3H_6} + 12H_2$$

8. **Reaction with halogens:** Diborane reacts with halogens to form the corresponding haloboranes. The reactivity with halogens decreases in the order: $Cl_2 > Br_2 > I_2$.

$B_2H_6 + 6Cl_2 \xrightarrow{25°C} 2BCl_3 + 6HCl$

9. **Reaction with halogen acids:** Diborane reacts with halogen acids to form the corresponding halodiborane. The reactivity with halogen acids increases in the order: HCl < HBr < HI.

$$B_2H_6 + HCl \xrightarrow{AlCl_3} \underset{\text{Chlorodiborane}}{B_2H_5Cl} + H_2\uparrow$$

$$B_2H_6 + HBr \xrightarrow{AlBr_3} \underset{\text{Bromodiborane}}{B_2H_5Br} + H_2\uparrow$$

$$B_2H_6 + HI \xrightarrow{\sim 323\,K} \underset{\text{Iododiborane}}{B_2H_5I} + H_2\uparrow$$

HCl and HBr react with diborane in the presence of their respective aluminium halides as catalyst, whereas HI react at ~ 323 K, in the absence of any catalyst.

10. **Reaction with alkali metals and their hyrides:** Formation of complex borohydrides.

$2B_2H_6 + Na \xrightarrow{Slow} Na^{\oplus}\,[BH_4]^{-} + Na^{\oplus}[B_3H_8]$

$B_2H_6 + NaH \longrightarrow \underset{\text{Sodium borohydride}}{Na^{\oplus}\,[BH_4]}$

These complex borohydrides are used as reducing agents in organic synthesis. They are also used as starting material for synthesis of other borohydrides.

11. **Reaction with CO:** B_2H_6 undergoes cleavage with Lewis basis to form gaseous borane carbonyl (or borane carbonyl) which is almost completely dissociated at 100°C.

$B_2H_6 + 2CO \rightleftharpoons 2[H_3B \leftarrow CO]$

12. **Hydroboration:** Diborane reacts with alkenes and alkynes forming alkylboranes when the reaction is carried out in dry ether, under an atmosphere of nitrogen (since B_2H_6 and the products formed are highly reactive).

$$RCH=CHR+\frac{1}{2}B_2H_6 \xrightarrow[N_2\ atm]{Dry\ ether} B(CH_2-CH_2R)_3+3RH$$

$$RC\equiv CR+\frac{1}{2}B_2H_6 \longrightarrow B(RC=CHR)_3$$

13. Reaction with methanol:

$$B_2H_6+6CH_3OH \longrightarrow 2B(OCH_3)_3+6H_2$$

14. Reaction with Et_2S:

$$B_2H_6+2Et_2S \longrightarrow 2[Et_2S \longrightarrow BH_3]$$

6.11.7 Structure and Bonding of Diborane

Boranes are one of the most important class of compounds, in which there are not enough valence electrons to form the conventional two-electron bonds between all the adjacent pair of atoms, so these compounds are known as electron-deficient compounds.

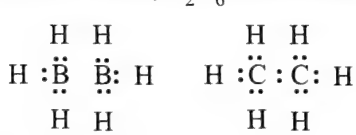
1. In diborane (B_2H_6), there are twelve valence electrons, i.e. three from each of the two boron atoms and one from each of the six hydrogen atoms.

   Number of valence electrons available in $B_2H_6 = 3\times 2+1\times 6=12$

   Whereas the number of electrons required to form ethane (C_2H_6) like structure are fourteen, i.e. four from each of the two carbon atoms and one from each of the six hydrogen atoms.

   Number of valence electrons available in $C_2H_6 = 4\times 2+1\times 6=14$

   Hence, B_2H_6 cannot have C_2H_6-like structure, i.e. unlike C_2H_6 which has C–C bond, B_2H_6 cannot have B–B bond.



2. Electron diffraction studies of B_2H_6 indicate the structure as given in Fig. 6.12.

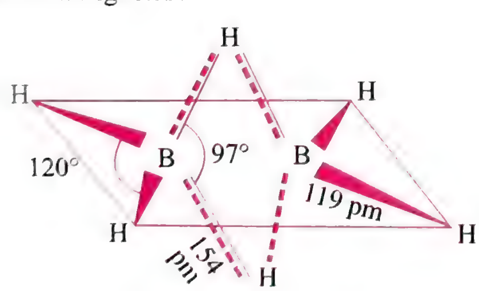


Fig. 6.12. Structure of B_2H_6

B_2H_6 has two types of hydrogen atoms:

a. **Terminal hydrogen atoms:** The four hydrogen atoms, i.e. two on the left and two on the right shown by thick lines are known as *terminal hydrogens*. The two B-atoms and four terminal H-atoms lie in the same plane, i.e. are coplanar.

b. **Bridge hydrogen atoms:** The remaining two hydrogen atoms, i.e. one lying above and one lying below the plane, form bridges and hence are known as *bridge hydrogens*.

The bridging hydrogen atoms prevent the free rotation between two B atoms. Specific heat measurement confirms that the rotation is hindered.

Presence of two different types of H atoms, i.e. four of one type and two of another type is also supported by the experimental fact that B_2H_6 cannot be methylated beyond $Me_4B_2H_2$ without breaking the molecule into BMe_3.

$$B_2H_6 \xrightarrow{Methylation} Me_2B_2H_2 \xrightarrow{Methylation} 2BMe_3$$

(Methylation – replacement of H atom by methyl, Me group)

Thus, there are two types of B–H bonds in B_2H_6:

i. The four terminal B–H bonds have same bond lengths as measured in non-electron deficient compounds. Hence they are normal covalent bonds, with two electrons shared between the two B and H atoms. These bonds are said to be *two centre two electron bonds (2c, 2e)* and thus are quite strong.

ii. The two bridge bonds, B–H–B, are much longer as compared to terminal B–H bonds and hence the electron deficiency must be associated with the bridge groups. These are abnormal bonds as two bridges involve only one electron from each B atom and one from each hydrogen atom making a total of four electrons. In other words, each B–H–B bond consists of two electrons delocalised over *three centres forming three centre two electron bonds (3c, 2e)* and hence are quite weak.

   Since they resemble banana, these (3*c*, 2*e*) bonds are also known as *banana bonds*.

The structure of diborane on the basis of hybridisation is shown in Fig. 6.13.

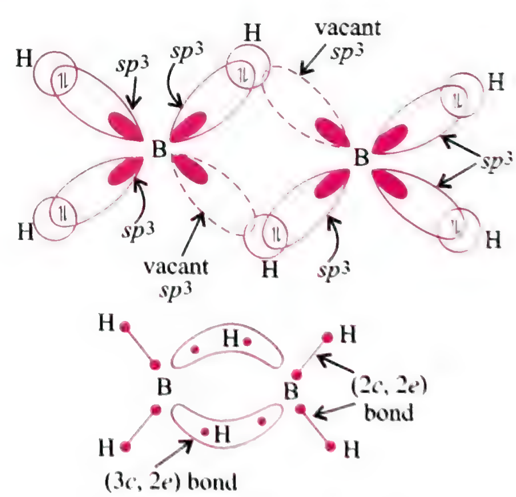


Fig. 6.13 Structure of diborane

B in B_2H_6 is sp^3 hybridised. The two half-filled sp^3 orbitals of each B atom overlap with the half-filled 1*s* orbital of H atom to form normal covalent bonds (2*c*, 2*e*). The third half-filled sp^3 hybrid orbitals of one of B-atom overlap simultaneously with half-filled 1*s* orbital of H atom and vacant sp^3 hybrid orbital

of the other B atom forming bridge bond, i.e. three centre two electron bond (3*c*, 2*e*). Thus B–H–B contains two electrons spread over three atoms. That is why this bond is known as (3*c*, 2*e*) bond.

ILLUSTRATION 6.11

Assuming that each has icosahedral structure, determine how many isomers are possible for the $B_{10}C_2H_{12}$ molecule?

Sol. Three isomers are possible. The carbon atoms may be at adjacent possible, may have one boron atom between them or may be on opposite side of the icosahedran. There are only three isomers possible because the 12 positions of the icosahedran are all inherently equivalent.

ILLUSTRATION 6.12

Diborane, B_2H_6, reacts with water to form boric acid and hydrogen. What is the pH of the solution which results when 1.104 g of B_2H_6 reacts with 100 mL water? Assume the final volume to be 100 mL.

Given: K_a of $H_3BO_3 = 8 \times 10^{-10}$, $pK_a = 9.1$; Atomic weight of B = 10.8 g; MW of $B_2H_6 = 27.6$ g mol^{-1}.

Sol. $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 2H_2$

1 mol 2 mol

27.6 g

27.6 g of B_2H_6 gives 2 moles of H_3BO_3

$$\therefore \text{ 1.104 g of } B_2H_6 \text{ gives} = \frac{2 \times 1.104}{27.6} = 0.08 \text{ mol}$$

Since 0.08 mol of H_3BO_3 is present in 100 mL (i.e. 0.1L), resulting molarity of H_3BO_3 solution is

$$\text{M of } H_3BO_3 = \frac{0.08 \text{ mol}}{0.1 \text{ L}} = 0.8 \text{ M}$$

Since H_3BO_3 is a weak acid, therefore pH of weak acid (i.e. pH_{WA}) is given by:

$$pH_{WA} = \frac{1}{2}(pK_a - \log C)$$
$$= \frac{1}{2}(9.1 - \log 0.8)$$
$$= \frac{1}{2}[9.1 - (-0.1)] = 4.6$$

$$\left[\begin{aligned} \log 0.8 &= \log 8 \times 10^{-1} \\ &= 3 \log 2 - 1 \\ &= 3 \times 0.3 - 1 \\ &= 0.9 - 1 \\ &= -0.1 \end{aligned}\right]$$

$\therefore$ pH of $H_3BO_3 = 4.6$

6.11.7.1 Structure of $Al_2(CH_3)_6$

In one terminal (CH_3) group only one (C–H) bond is lying in one plane with Al atom = 2 atoms (C and H).

In four terminal (CH_3) groups, number of atoms lying in one plane with Al atom = 2 × 4 = 8 atoms.

Two Al atoms are also in plane with 8C and 8H atoms in four terminal (CH_3) group.

Thus, maximum number of atoms that lie in plane having terminal (Al–CH_3) bonds = 8 + 2 = 10.

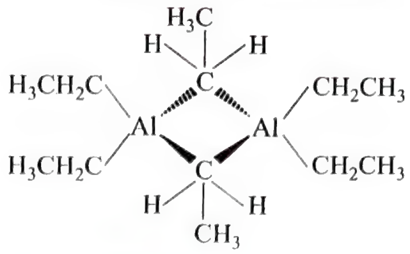


ILLUSTRATION 6.13

Consider the structure of $Al_2(CH_3)_6$.

If P = Total number of ($3C - 2e^-$) bonds.

Q = Total number of atoms that are sp^3 hybridised.

R = Maximum number of atoms that can lie in plane having terminal (Al–CH_3) bonds.

Then the value of $\frac{R-P}{Q}$ is

Sol. (1) Refer to the structure of $Al_2(CH_3)_6$.

$P = (3C - 2e^-)$ bonds = 2

All six C-atoms and two Al atoms are sp^3 hybridised.

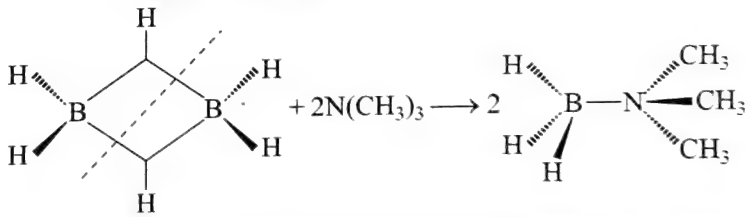
$\therefore Q = 8$.

R = Maximum number of atoms that can lie in plane having terminal (Al–CH_3) bonds = 10.

$$\text{Thus, } \frac{R-P}{Q} = \frac{10-2}{8} = 1$$

6.11.7.2 Symmetric and Unsymmetric Cleavage of B_2H_6 (diborane)

(a) (i) In symmetric cleavage, B_2H_6 is broken symmetrically into two BH_3 fragments each of which forms a complex with Lewis base.



Many complexes of this kind exist. They are isoelectronic with hydrocarbons. The above product is isoelectronic with 2,2-dimethyl propane [neopentane, $C(CH_3)_4$].

(ii) **Soft and bulky Lewis bases** (L) cleave diborane symmetrically giving $H_3B.Lx$. Although B_2H_6 reacts with many hard Lewis bases, it is best regarded as a soft Lewis acid.

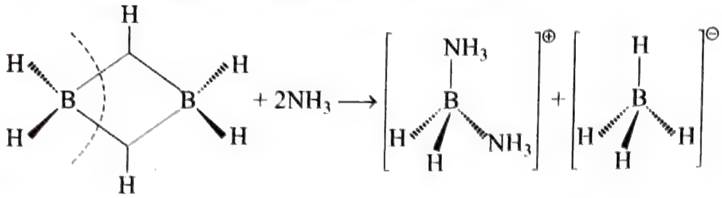
B_2H_6 reacts symmetrically with CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, CO, PF_3, Pyridine etc.

(iii) $H_3BN(CH_3)_3 + F_3BS(CH_3)_2 \longrightarrow H_3BS(CH_3)_2 + F_3BN(CH_3)_3$

Stability trends indicates that BH_3 is a soft Lewis acid (as shown in above example ii) in which BH_3 transfers to the soft S donor atom and the harder Lewis acid, BF_3 combines the hard N donor atoms.

(b) Unsymmetric cleavage: This kind of cleavage is generally observed when B_2H_6 reacts with strong, sterically uncrowded bases at low temperature. The steric repulsion is such that only two small ligands can attack one B atom in the course of the reaction.

The direct reaction of B_2H_6 and NH_3 results in *unsymmetrical cleavage* resulting to an ionic product.



More compact and hard Lewis bases cleave the hydrogen bridge unsymmetrically giving $[H_2BL_2]^{\oplus}[BH_4]^{\ominus}$

(c) Summary of some reactions of diborane:

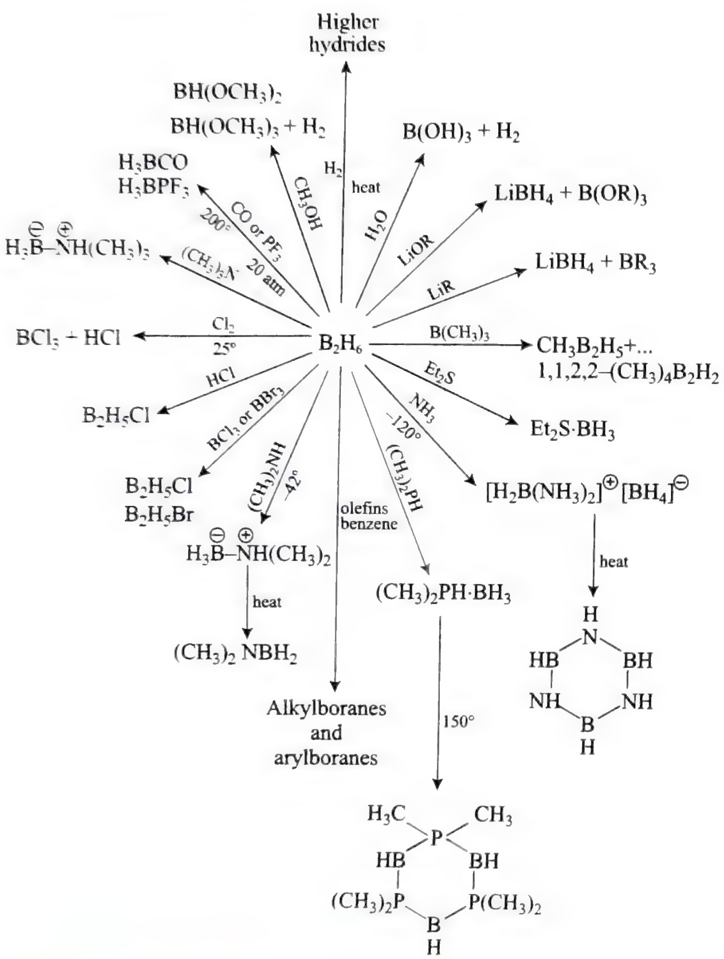


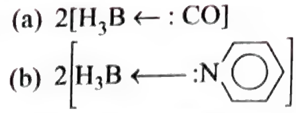
ILLUSTRATION 6.14

When B_2H_6 is allowed to react with following Lewis bases, then how many given Lewis bases form adduct through *symmetrical cleavage* of B_2H_6?

CO	Pyridine	Tetra hydro furan (T.H.F.)	
(a)	(b)	(c)	
PH_3	PF_3	$(CH_3)_3N$	$(CH_3)_2NH$
(d)	(e)	(f)	(g)
NH_3	CH_3NH_2		
(h)	(i)		

Sol. (6) Soft and bulky Lewis bases (L) cleave B_2H_6 symmetrically giving $H_3B.Lx$ (a), (b), (e), (f), (g) and (i) form adduct through symmetrical cleavage of B_2H_6.

(a) $2[H_3B \leftarrow :CO]$



(e) $2[H_3P \leftarrow :PF_3]$

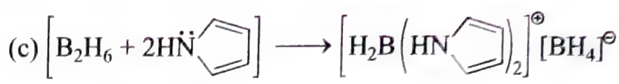
(f) $H_3B^{\ominus} - N^{\oplus}(CH_3)_3$

(g) $H_3B^{\ominus} - NH^{\oplus}(CH_3)_2$

(i) $H_3B^{\ominus}\ NH^{\oplus}_2(CH_3)$

With (c), (d) and (h), B_2H_6 react unsymmetrically to form ionic product.

Note: Pyridine is stronger base than THF, due to non-delocalization of lone pair e^-*'s* on N-atom in pyridine. In THF, lone pair e^-*'s* are delocalized via resonance.



(d) $B_2H_6 + 2PH_3 \rightarrow [H_2B(PH_3)_2]^{\oplus}[BH_4]^{\ominus}$

(h) $B_2H_6 + 2NH_3 \rightarrow [H_2B(NH_3)_2]^{\oplus}[BH_4]^{\ominus}$

6.11.8 Boron Carbide, B_4C

It is a covalent carbide.

Preparation:

(i) $2B_2O_3 + 7C \xrightarrow{2500°C} B_4C + 6CO$

(ii) By dissolving C and B in certain metals like Cu or Ag in an electric furnance. The molten mass is then treated with HNO_3 to dissolve the metal.

Properties: It is black lusturous compound. It is harder than SiC and is electric conductor.

Structure: Unit cell of B_4C contains three B_4C molecules and hence formula can be $B_{12}C_3$.

Icosahedral of 12 B-atoms are linked with linear C_3-chains.

In icosahedral B_{12} unit, 12 B-atoms link together, to form an icosahedron and separate B atoms link together the B_{12} units.

The structural units of linear chains of 3 C-atoms and B_{12} groups are arranged at the vertices of a regular icosahedral. Each B-atom is bonded to five other B-atoms in the same B_{12} groups producing a 3D boron network.

A carbon at the end at a C-chain is attached to the central C-atom and to 3B-atoms. The central C-atom is attached only to other 2C-atoms of the chain.

Uses:

(i) For cutting diamonds

(ii) Hardest abrasive and better than SiC.

(iii) Drilling holes in rockets.

(iv) For making lamp filaments.

(v) For making electrodes for electric furnances.

6.11.9 Borazines

Boron nitrogen species carrying only one substituent on each atom, which exist as trimers $(XBNR)_3$ are called borazines. Borazine is $B_3N_3H_6$ (colourless, volatile liquid) and is also known as inorganic benzene.

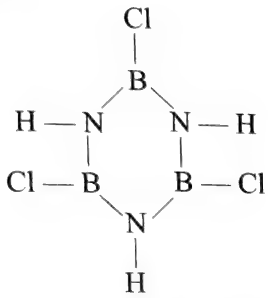
Preparation:

1. By heating B_2H_6 and NH_3 in 1:2 molar ratio at –120°C, which gives diammoniate of diborane (which is an additional compound), this compound on heating at 200°C gives borazine.

$$B_2H_6 + 2NH_3 \xrightarrow{-120°C} [H_2B(NH_3)_2]^{\oplus}[BH_4]^{\ominus} \xrightarrow{200°C} B_3N_3H_6 + 6H_2$$

2. By heating BCl_3 and NH_4Cl in chlorobenzene at 140°C in the presence of Fe, Ni or Co as catalyst.

$$3BCl_3 + 3NH_4Cl \xrightarrow[140°C,\ Fe]{C_6H_5Cl}$$



$+ 9HCl$

The product (B, B, B-trichloroborazine) is then reduced by $NaBH_4$ in polyether, which gives borazine.

$\downarrow$ + 6$NaBH_4$ + Polyether

$$2B_3N_3H_6 + 6NaCl + 3B_2H_6$$

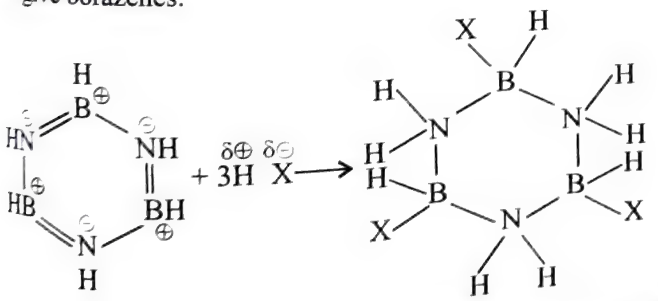
Borazine

3. By heating $LiBH_4$ and NH_4Cl at 275°C.

$$3LiBH_4 + 3NH_4Cl \xrightarrow{275°C} B_3N_3H_6 + 3LiCl + 9H_2$$

Properties:

1. Borazine nucleus readily undergoes addition reaction with molecules containing acidic hydrogen atoms such as hydrogen halides, water, methanol and carboxylic acids to give borazenes.



In the addition reaction with borazine, the more electronegative half of the attacking molecule (HX) gets attached to the boron atoms, probably because the boron atoms in borazine are positively charged relative to the nitrogen as boron is less electronegative as compared to nitrogen.

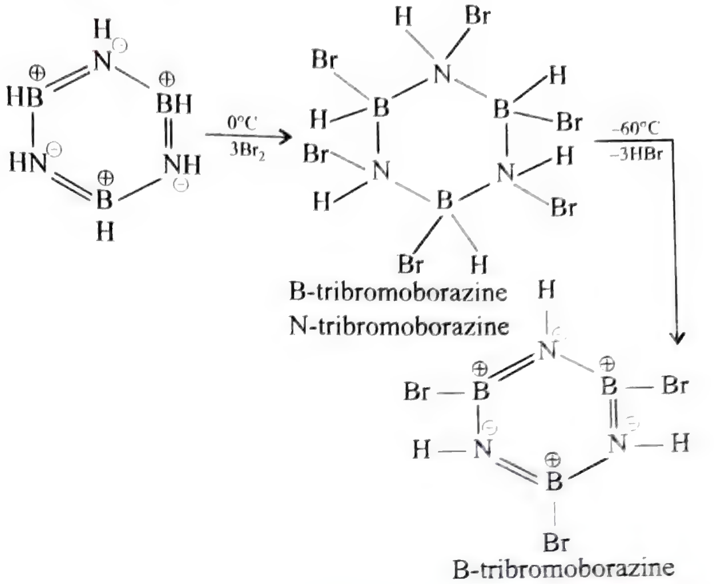
2. Reaction with water: Borazine gets slowly hydrolysed by water to produce H_2, boric acid and ammonia (NH_3). Hydrolysis is favoured by the increase in temperature.

$$B_3N_3H_6 + 9H_2O \longrightarrow 3NH_3 + 3H_3BO_3 + 3H_2$$

Under controlled conditions, hydrolysis yields $(OH)_3B_3N_3H_6$.

$$B_3N_3H_6 + 3H_2O \longrightarrow (HO)_3B_3N_3H_6 + 3H_2\uparrow$$

3. Reaction with Br_2:



6.11.10 Structure and Bonding of Borazines

Borazine is also known as *inorganic benzene*, due to its similarity with benzene (C_6H_6) (only physical properties).

Borazine is isoelectronic and isosteric with benzene.

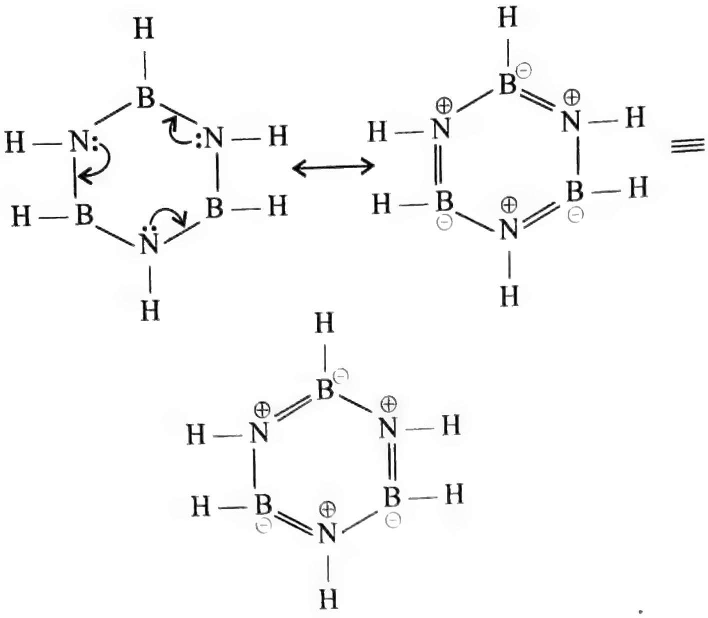
1. Number of electrons in borazine, $B_3N_3H_6$
   $= 5$ from each B + 7 from each N + 1 from each H
   $= 5 \times 3 + 7 \times 3 + 1 \times 6 = 42$
   Number of electrons in benzene, C_6H_6
   $= 6$ from each C + 1 from each H
   $= 6 \times 6 + 1 \times 6 = 42$
   Since the number of electrons in borazine and benzene are same, borazine is isoelectronic (i.e. same number of electrons) with benzene.
2. Number of atoms in borazine, $B_3N_3H_6$
   = 3 atoms of B + 3 atoms of N + 6 atoms of H = 12 atoms
   Number of atoms in benzene, C_6H_6
   = 6 atoms of C + 6 atoms of H = 12 atoms
   Since the total number of atoms in borazine and benzene are same, borazine is isosteric with benzene.

The molecular structure of borazines has been determined by diffraction methods. The data show that :

1. Borazines possess a cyclic structure of alternating boron and nitrogen atoms. All the atoms in the ring lie in a plane.
2. d(B–N; in borazine) = 1.42 Å
   d(B–N; in $R_3B \leftarrow NR_3$) = 1.60 Å

B–N bond distance in borazine is considerably shorter than B–N bond distance in boron nitrogen adduct; moreover, all the B–N distances in the ring are equal.

These results suggest that the borazine cyclic trimer is best described as containing B–N multiple bond rather than B–N single bond.



Presumably, all the ring atoms (i.e. 3B and 3N atoms) use sp^2 hybridised orbitals to form three σ bonds.

The electron pair present in the $2p_z$ orbitals of N forms π-bond by the lateral overlap with vacant $2p_z$ orbital of B atom.

Borazine is isoelectronic to benzene, both the compounds have aromatic π-clouds of electron density which is delocalised over the atoms of the ring. Although some properties (physical) of borazine and benzene are similar, their chemical properties are markedly different. In benzene (C_6H_6), C=C bonds are non-polar; while in borazine ($B_3N_3H_6$), due to the difference in electronegativity between B and N, B–N bond is polar $(\overset{\delta+}{B}-\overset{\delta-}{N})$ and hence π-electron cloud in $B_3N_3H_6$ is lumpy with more electron density localised on N atom. The partial localisation of electron density on N atoms, weakens the π-bond in the ring because of which borazine undergoes addition reaction with polar species such as HCl, while benzene does not undergo addition reaction.

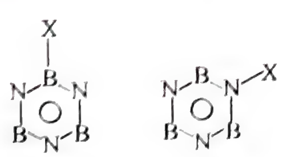
Non-polar Polar

ILLUSTRATION 6.15

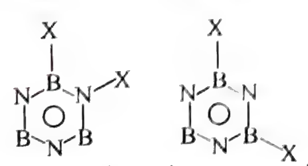
How many isomers are possible for the following compounds of borazole (a) $B_3N_3H_5X$ (b) $B_3N_3H_4X_2$ and (c) $B_3N_3H_3X_3$?

Sol.

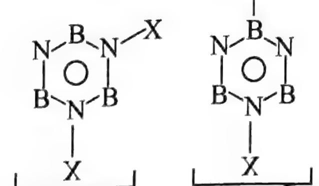
a. 2-isomers:



b. 4-isomers:



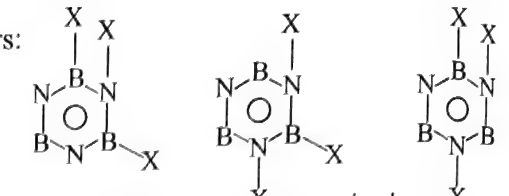
o = Ortho m = Meta



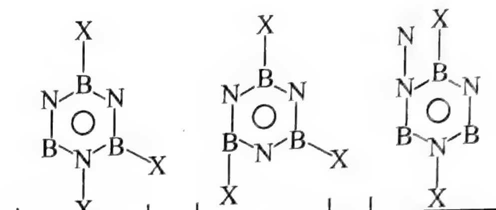
m = Meta p = Para

o ⇒ 1
m = 2
p = 1
Total = 4

c. 6-isomers:



A A U



U S S

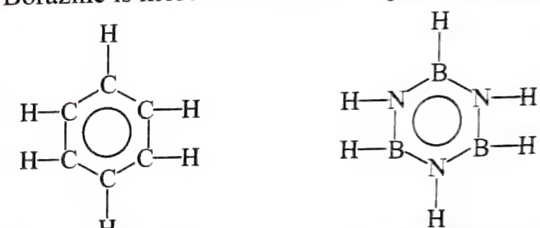
A = 2
U = 2
S = 2
Total = 6

(A ⇒ Adjacent; U ⇒ Unsymmetrical; S ⇒ Symmetrical)

ILLUSTRATION 6.16

Benzene or borazine, which is more reactive and why?

Sol. Borazine is more reactive as compared to benzene.



Benzene (C_6H_6) Borazine ($B_3N_3H_6$)

Benzene (C_6H_6) which consists of C=C bonds is a non-polar molecule, whereas borazine ($B_3N_3H_6$) having B–N bonds, due to electronegativity difference between B and N atoms (B is less electronegative as compared to N) is a polar molecule ($B^{\delta-}-N^{\delta+}$). Hence, the π-cloud in $B_3N_3H_6$ is more lumpy, i.e. having more electron density on N as compared to B. This partial localisation of electron density on N atoms weakens the B–N bond making barazine more reactive as compared to benzene.

6.11.11 Boron Nitride $(BN)_x$

Preparation:

1. By heating boron to white heat in an atmosphere of N_2 or NO at 1000°C.

   $2B + N_2 \longrightarrow 2(BN)$

   $5B + 3NO \longrightarrow 3BN + B_2O_3$

2. By fusing a mixture of anhydrous borax ($Na_2B_4O_7$) and ammonium chloride in a platinum crucible.

   $Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2NaCl + 2BN + B_2O + 4H_2O$

   The resulting mass is treated with dil HCl in which NaCl and B_2O_3 are soluble leaving behind BN, an insoluble residue.

3. By heating borazine at 200°C.

$$B_3N_3H_6 \xrightarrow{200°C} 2BN + 3H_2$$

4. By heating B_2O_3 with $Hg(CN)_2$, KCN or NH_4Cl.

$$B_2O_3 + Hg(CN)_2 \longrightarrow 2BN + CO + CO_2 + Hg$$

$$B_2O_3 + 2KCN \longrightarrow 2BN + K_2O + 2CO$$

$$B_2O_3 + 2NH_4Cl \longrightarrow 2BN + 3H_2O + 2HCl$$

Properties:

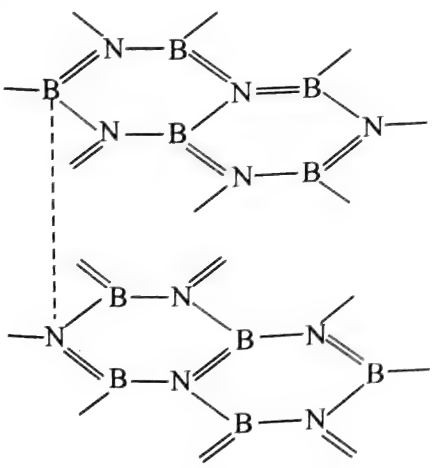
1. Boron nitride melts under pressure at 3000°C. It is very stable and unreactive. It remains unaffected by mineral acids, solution of alkali and Cl_2 at red heat.
2. It decomposes when:
   a. Fused with KOH:
   $$BN + 3KOH \longrightarrow K_3BO_3 + NH_3$$
   b. Heated in steam under presure:
   $$2BN + 3H_2O \longrightarrow B_2O_3 + 2NH_3$$
3. BN dissolves in HF (slowly).
   $$BN + 4HF \longrightarrow NH_4BF_4 \text{ (Ammonium borofluoride)}$$
4. BN fuses with K_2CO_3.
   $$BN + K_2CO_3 \longrightarrow \underset{\text{Potassium metaborate}}{KBO_2} + \underset{\text{Potassium cyanate}}{KCNO}$$

6.11.12 Structure and Bonding of Boron Nitride

Boron nitrides can be expected to occur in two forms. The form normally obtained from the usual preparative procedures exhibit a layer-like structure (like graphite) and the other form consists of giant three-dimensional lattice (like diamond).

In the graphite-like structure, the bonding within the layers is by sp^2 hybrids of both B and N, the remaining unhybridised orbitals (filled 2p of N and vacant 2p of B) form the delocalised π-bonding.

Like graphite, the compound is a good lubricant, there being only van der Waals interaction between the layers which are 3.30 Å apart.



d(B – N) = 1.45 Å

Interlayer distance = 3.30 Å

The structure differs from that of graphite in having the hexagons directly over one another (B under N). Unlike graphite, BN is a white solid and an insulator.

6.11.13 Aluminium Oxide or Alumina

Alumina, Al_2O_3, occurs in nature as colourless corundum and tinted with metallic oxides as ruby (red), sapphire (blue), amethyst (violet), emery (green) etc. These coloured oxides are precious stones. Hydrated oxide ($Al_2O_3 \cdot 2H_2O$) occurs as bauxite.

Preparation:

1. By igniting aluminium hydroxide, $Al(OH)_3$; aluminium sulphate, $Al_2(SO_4)_3$; or ammonium alum.
   $$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$
   $$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$
   $$Al_2(SO_4)_3 \longrightarrow Al_2O_3 + 3SO_2$$
   $$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \longrightarrow Al_2O_3 + 2NH_3 + 4SO_3 + 25H_2O$$
2. It is obtained in crystalline form by strongly heating a mixture of aluminium fluoride, AlF_3, and boric oxide, B_2O_3.
   $$2AlF_3 + B_2O_3 \longrightarrow Al_2O_3 + 2BF_3$$

Properties:

1. White solid, insoluble in water.
2. Stable and unreactive substance.
3. Al_2O_3 begins to volatilise at 1750°C and melts at 2050°C. It boils at 2250°C.

Uses:

1. For the manufacture of aluminium.
2. As a refractory material, for making heat-resistant bricks for lining furnaces.
3. When it is heated in an electric arc at 3000°C, a hard powder, 'alundun' is obtained, which is used as an abrasive.
4. Bauxite cement, which is made by fusing bauxite and lime, is not affected by sea water and sets quickly.
5. As a medium, in chromatography.
6. In preparing precious stones.

6.11.14 Aluminium Chloride ($AlCl_3$ or Al_2Cl_6)

Preparation:

1. **Anhydrous aluminium chloride:**
   a. By passing dry HCl gas or Cl_2 gas over heated Al turnings in absence of air. The vapours of aluminium chloride are condensed when solid anhydrous aluminium chloride is obtained.
   $$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$
   $$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$
   b. By heating a mixture of alumina and carbon in an atmosphere of chlorine.
   $$Al_2O_3 + 3C + 3Cl_2 \xrightarrow{1000°C} \underset{\text{Vapours}}{2AlCl_3} + 3CO$$
   Vapours of $AlCl_3$ are cooled to obtain solid anhydrous aluminium chloride.
2. **Hydrated aluminium chloride:** $AlCl_3 \cdot 6H_2O$ is obtained by dissolving aluminium metal or aluminium hydroxide in dil HCl.

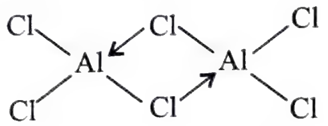
$2\,Al + 6HCl \longrightarrow 2\,AlCl_3 + 3H_2\uparrow$

$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$

HCl gas is circulated through the solution to obtain crystals of hydrated aluminium chloride.

Properties:

1. Anhydrous aluminium chloride: White solid.
   a. Deliquescent and fumes in air.
   b. On heating, it sublimes at 180°C and vapour density corresponds to the formula Al_2Cl_6.
   c. It is covalent when anhydrous as it does not conduct electricity in fused state.
   d. It is soluble in organic solvents such as alcohol, ether etc.
   e. The dimeric form, Al_2Cl_6, is retained in non-polar solvents but is broken in $[Al(H_2O_6)]\,Cl_3$ on dissolution in water on account of high heat of hydration. The molecule (dimer) is an autocomplex and is representated as follows.



2. Anhydrous aluminium chloride fume in moist air due to evolution of HCl.

$Al_2Cl_6 + 6H_2O \longrightarrow 2Al(OH)_3 + 6HCl\uparrow$

3. Anhydrous aluminium chloride, on dissolving in water, changes into hydrated aluminium chloride which is ionic in nature.

$Al_2Cl_6 + 12H_2O \longrightarrow 2AlCl_3{\cdot}6H_2O$

$AlCl_3.6H_2O \xrightarrow{\text{Dissociation}} [AlCl_2(H_2O)_4]^{\oplus} + [AlCl_4(H_2O)_2]^{\ominus}$

4. The solution of aluminium chloride in water is acidic in nature due to hydrolysis.

$$\underset{}{AlCl_3} + 3H_2O \longrightarrow \underset{\text{Weak base}}{Al\,(OH)_3} + \underset{\text{Strong acid}}{3HCl}$$

5. When NH_4OH is added to solution of ammonium chloride, a geletinous white precipitate of aluminium hydroxide is obtained, which does not dissolve in excess of NH_4OH.

$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3 + 3NH_4Cl$

6. When sodium hydroxide (NaOH) is added to the solution of aluminium chloride drop by drop, a white geletinous precipitate of aluminium hydroxide, $Al(OH)_3$, is formed which dissolves in excess of NaOH forming sodium meta-aluminate ($NaAlO_2$).

$AlCl_3 + 3NaOH \longrightarrow Al\,(OH)_3 + 3NaCl$

$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$

7. $Al(OH)_3$ dissolves in NaOH to give $[Al(OH)_4]^{\ominus}$ Ion which is supposed to the octahedral complex species $[Al(OH)_4(H_2O)_2]^{\ominus}$ In aqueous solution.

$Al(OH)_3 + NaOH(aq) \longrightarrow [Al(OH)_4(H_2O)_2]^{\ominus}(aq) + Na^{\oplus}(aq)$

($AlCl_3$) sublimes on heating at 180°C under vacuum.

Uses:

1. As a catalyst in Friedel–Crafts reaction.
2. In the manufacture of dyes, drugs and perfumes.

6.11.15 ULTRAMARINES

It is an artificial lapis lazuli. Lapis lazuli is a rare mineral which has fine blue colour. It is a complex silicate of sodium and aluminium containing 12% of sulphur probably in the form of sodium sulphide. It can be prepared artificially by heating a mixture of Kaolin, soda and sulphur and charcoal to bright red heat. Initially, a white mass is formed which changes to green mass in air. It is powdered and heated with more of sulphur, where a blue variety with composition $Na_5Al_3Si_3S_2O_{12}$ is obtained. Blue variety on heating in a current of dry chlorine changes to violet variety.

Blue variety is the most common and is used in (i) making blue paint; (ii) making wall paper and blue tinted paper; (iii) calico printing and (iv) laundry for blueing purposes.

6.11.16 ALUMS

Initially, the term alum was used only for potassium aluminium sulphate, $K_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$, a double sulphate with 24 molecules of water of crystallisation. But now this term is used for all double sulphates having composition:

$$\overset{\text{I}}{M}_2SO_4 \cdot \overset{\text{III}}{M}_2(SO_4)_3 \cdot 24H_2O,$$

where $\overset{\text{I}}{M}$ stands for monovalent basic radicals such as $Na^{\oplus}$, $K^{\oplus}$, $Pb^{\oplus}$, $Cs^{\oplus}$, $Ag^{\oplus}$, $Tl^{\oplus}$ and $NH_4^{\oplus}$.

$\overset{\text{III}}{M}$ stands for trivalent basic radicals such as Al^{3+}, Cr^{3+}, Fe^{3+}, Mn^{3+}, Co^{3+}, etc.

Examples:

Potash alum	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
Chrome alum	$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$
Ferric alum	$(NH_4)_2\,SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$

1. Alums are generally obtained by mixing hot solutions of equimolar qualities of their constituent sulphates and subjecting the resulting solution to crystallisation.
2. Alums are crystalline compounds.
3. In alums, each metal is surrounded by six water molecules and the crystals of alums consist of $[M(H_2O)_6]^{\oplus}$, $[M(H_2O)_6]^{3+}$ and SO_4^{2-} ions.
4. Alums are fairly soluble in hot water but less soluble in cold water.
5. The solution of alum in water is acidic and have stringent taste.
6. The solution of alum in water shows the properties of the constituent salts.
7. The alums are isomorphous to each other and form mixed crystals.
8. Each alum has different melting point.

9. Alums lose water of crystallisation when heated.
10. On rapid heating to a high temperature, the alum swells up and a porous mass, *burnt alum* is left behind. It is commonly known as *alum*.

Preparation:

1. **From bauxite:** Bauxite is boiled with H_2SO_4 to form aluminium sulphate, $Al_2(SO_4)_3$. To this solution, calculated quantity of K_2SO_4 is added. The resulting solution is concentrated and cooled. After sometime, crystals of potash alum are obtained.

$$\underset{\text{Bauxite}}{Al_2O_3} + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$$

$$Al_2(SO_4)_3 + K_2SO_4 + 24H_2O \longrightarrow \underset{\text{Potash alum}}{K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O}$$

2. **From alum stone or alunite:** Alum stone is treated with dil H_2SO_4 and the solution is boiled. A calculated quantity of K_2SO_4 is added to the solution. The solution on cooling yields crystals of potash alum.

$$\underset{\text{Alum stone or alunite}}{K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3} + 6H_2SO_4 \longrightarrow K_2SO_4 + 3Al_2(SO_4)_3 + 12H_2O$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$

Properties:

1. White crystalline compound.
2. It is soluble in water and its aqueous solution is acidic due to hydrolysis of $Al_2(SO_4)_3$.

$$Al_2(SO_4)_3 + 6H_2O \longrightarrow \underset{\text{Weak base}}{2Al(OH)_3} + \underset{\text{Strong acid}}{3H_2SO_4}$$

3. On heating, it swells on account of elimination of water molecules.

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \xrightarrow{200°C} K_2SO_4 \cdot Al_2(SO_4)_3 + 24H_2O$$

$$K_2SO_4 \cdot Al_2(SO_4)_3 \xrightarrow{\text{Red heat}} K_2SO_4 + Al_2O_3 + 3SO_3$$

4. Its aqueous solution contains $K^{\oplus}$, Al^{3+} and SO_4^{2-} ions and their usual tests can be performed.

Uses:

1. As a mordant (a compound that helps to attach the dye to the fabric) in dyeing and calico printing.
2. In leather tanning.
3. In purification of water.
4. In sizing of cheap quality of paper.

6.11.17 Pseudo Alums

Double sulphates of divalent ions and trivalent ions with 24 water molecules of crystallisation are known as pseudo alums, $\overset{+2}{M}SO_4 \cdot M_2^{+3}(SO_4)_3 \cdot 24H_2O$. These are not isomorphous with alums.

6.12 USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS

1. **Boron:** Boron is an extremely hard refractory solid with high melting point, low density and very low electrical conductivity. Thus, it finds many applications. Some of these applications are as follows:
   a. Boron is used to make impact resistant steel, as it increases the hardenability (i.e. the depth to which it will harden) of steel.
   b. Boron fibres have high tensile strength and thus are used to make bullet proof vests and light composite material for aircrafts.
   c. Boron-10 ($^{10}_{5}B$) isotope has high ability to absorb neutrons and therefore metal borides are used in nuclear industry as protective shields and control rods.
   d. Borax ($Na_2[B_4O_5(OH)_4] \cdot 8H_2O$) and boric acid ($B(OH)_3$) are used in the manufacture of heat-resistant glasses (e.g. pyrex), glass-wool and fibre glass.
   e. Borax is also used as flux for soldering metals for heat, scratch and stain-resistant glazed coating to earthenware and as a constituent of medicinal soaps.
   f. An aqueous solution of boric acid is generally used as an antiseptic.
   g. Borax is used as flame retardant for fabric and wood, and mixed with NaOH and sold as 'Polybor' and 'Timbor' for treating timber and hardboard against the attack by woodboring insects.
   h. Borax is also used in making enamel and in leather tanning.
   i. Boron sesquioxide (B_2O_3) is used in making borosilicate (heat resistant) glass (e.g. pyrex, which contains 14% B_2O_3). Borosilicate glass has a lower coefficient of thermal expansion and is easier to work than normal 'soda glass'. H_3BO_3, B_2O_3 and calcium borate are used to make soda free glass fibre, which is used for thermal insulation in houses.
2. **Aluminium:** Aluminium is a bright, silvery white metal with high tensile strength. Its main advantage is its lightness. (low density = 2.73 g cm^{-3}). Some of its applications are as follows:
   a. Since aluminium is light and good conductor of electricity (on a weight for weight basis they conduct twice as well as copper), it is used to make electric power cables.
   b. Finely divided aluminium powder is called 'aluminium bronze', and is used in preparing *aluminium paint* for protection of iron and zinc. Aluminium powder mixed

with linseed oil shines like silver and thus is also known as *silver paint*.

c. Aluminium powder is used as a reducing agent in aluminothermic process for extraction of chromium and manganese from their ores.

d. Aluminium powder is used in flash light bulbs for indoor photography.

e. Aluminium is converted into alloys. Some important alloys of aluminium and their uses are given below:

Alloy	Composition	Uses
Duralumin	Al 95% Cu 4% Mn 0.5% Mg 0.5%	To make aeroplanes, automobile parts, pressure cooker etc. as it is light, tough, ductile and resistant to corrosion.
Magnalium	Al 95% Mg 5%	To make light instruments, pressure cookers etc. as it is light, tough and strong.

f. Since aluminium is a cheap metal which resists corrosion, it is used for making cooking utensils, cans for drinks, tubes for toothpaste, picture frame, etc. However, the use of aluminium and its compounds for domestic purposes is now reduced considerably due to its toxic nature.

g. Aluminium foil is used for wrapping fine articles such as photographic films, pharmaceutical products, etc.

h. Aluminium hydroxide, $Al(OH)_3$, is used as an antacid for treatment of indigestion.

i. Potash alum, $K_2SO_4 \cdot Al(SO_4)_3 \cdot 24H_2O$ is used for the purification of water, as styptic for stopping bleeding, as mordant for dyeing, for tanning of leather, in calico printing and sizing of paper.

j. Anhydrous $AlCl_3$ is used as a catalyst in Friedel–Crafts reaction and in cracking of petroleum. Hydrated $AlCl_3$ is used as a mordant in dyeing.

6.12.1 Goldschmidt's Alumino-Thermic Process

As aluminium has great affinity for oxygen at high temperature, it has power to displace elements less electropositive than itself from their oxides. The reaction being so strongly exothermic that the metal set free is obtained in the molten condition and it is protected from oxidation by a layer of fluid slag consisting of Al_2O_3.

$$\text{Metal oxide} + Al \longrightarrow \underbrace{Al_2O_3 + \text{metal}}_{\text{Molten state}} + \text{Energy}$$

The reaction forms the basis of alumino-thermic process. It was discovered by Goldschmidt. The process has two main applications:

1. **Extraction of metals and non-metals:** The metals, e.g. Cr, Mo, Mn and non-metals such as B, Si etc. can be extracted from their corresponding oxides.

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr + \text{Energy}$$
$$3Mn_3O_4 + 2Al \longrightarrow 9Mn + 4Al_2O_3 + \text{Energy}$$
$$B_2O_3 + 2Al \longrightarrow 2B + Al_2O_3 + \text{Energy}$$
$$3SiO_2 + 4Al \longrightarrow 3Si + 2Al_2O_3 + \text{Energy}$$

The oxide is mixed with aluminium powder, the mixture thus obtained is ignited in a fire clay crucible surrounded by sand with the help of a catridge (containing Mg powder and barium peroxide, BaO_2). The large amount of heat produced in the reaction fuses both the alumina and the element set free. Two distinct layers are formed which are easily separated.

2. **Thermite welding of metals especially steel:** The broken parts to be welded is surrounded by a mould of sand and clay and heated to redness by means of a gasoline torch or a blast lamp. *Thermite,* i.e. mixture of Al powder and Fe_2O_3 in the ratio of 1:3 is taken in a crucible lined with a mixture of Mg powder and barium peroxide, BaO_2, with a Mg ribbon inserted into it. The thermite is ignited with Mg ribbon. Iron oxide is reduced to iron and temperature rises to about 2500°C. Molten iron thus produced is tapped into the parts to be welded. The heated surface of the broken iron melts and mingles with the molten iron, thus giving a perfect weld.

6.12.2 Extraction of Aluminium

In the metallurgy of aluminium, purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (fluorspar) which lowers the melting point of the mixture and increases conductivity. The fused matrix is electrolysed. Carbon cathode and graphite anode are used. The graphite anode is useful here for reduction to the metal. The overall reaction may be taken as $2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$. This process of electrolysis widely known as *Hall-Heroult* process.

The electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrons. The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2. This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away. The electrolytic reactions are:

At cathode: $Al^{3+}_{(melt)} + 3e^- \longrightarrow Al_{(l)}$

At anode: $C_{(s)} + O^{2-}_{(melt)} \longrightarrow CO_{(g)} + 2e^-$

$C_{(s)} + 2O^{2-}_{(melt)} \longrightarrow CO_{2(g)} + 4e^-$

Illustration 6.17

Why is boric acid considered as a weak acid?

Sol. $B(OH)_3 + H_2O \rightleftharpoons [B(OH)_4]^{\ominus} + H^{\oplus}$

Boric acid is not able to release $H^{\oplus}$ ion on its own. It receives $\overset{\ominus}{O}H$ ions from water molecule to complete its octet and in turn releases $H^{\oplus}$ ions.

ILLUSTRATION 6.18

Identify (X) and (Y) in the following reactions:

Colemanite + (X) $\longrightarrow Na_2B_4O_7$

$Na_2B_4O_7$ + (Y) $\longrightarrow H_3BO_3$

Sol. Colemanite ($Ca_2B_6O_{11}$) reacts with Na_2CO_3 to produce $Na_2B_4O_7$, which on acidification with hot and conc H_2SO_4/ HCl gives boric acid, H_3BO_3.

$$\underset{}{Ca_2B_6O_{11}} + \underset{(X)}{Na_2CO_3} \longrightarrow Na_2B_4O_7 + 2NaBO_2 + 2CaCO_3$$

$$Na_2B_4O_7 + \underset{(Y)}{H_2SO_4} + 5H_2O \longrightarrow 2Na_2SO_4 + 4H_3BO_3$$

Or

$$Na_2B_4O_7 + \underset{(Y)}{2HCl} + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$$

Hence, (X) is Na_2CO_3 and (Y) is H_2SO_4 or HCl.

ILLUSTRATION 6.19

Starting from boric acid prepare:

a. Boric anhydride
b. Boron trichloride
c. Boron trifluoride
d. Metaboric acid
e. Ethyl borate

Sol.

a. On strong heating, boric acid gives boric anhydride.

$$2H_3BO_3 \xrightarrow{\text{Red hot}} \underset{\text{Boric ahydride}}{B_2O_3} + 3H_2O$$

b. Boric acid is first converted to boric anhydride, B_2O_3. B_2O_3 is then mixed with carbon and the mixture is heated in a current of chlorine when boron trichloride, BCl_3 is formed.

$$2H_3BO_3 \xrightarrow{\text{Red hot}} B_2O_3 + 3H_2O$$

$$B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO$$

c. Boron triflurode, BF_3, is prepared by heating boric acid with CaF_2 and conc H_2SO_4.

$$2H_3BO_3 + 3CaF_2 + 3H_2SO_4 \longrightarrow 2BF_3\uparrow + 3CaSO_4\downarrow + 6H_2O$$

d. H_3BO_3 when heated at 100°C, decomposes to give metaboric acid.

$$H_3BO_3 \xrightarrow{100^\circ C} \underset{\text{Metaboric acid}}{HBO_2} + H_2O$$

e. By heating boric acid with ethyl alcohol in the presence of conc H_2SO_4, ethyl borate is formed. (Conc H_2SO_4 acts as dehydrating agent.)

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{H_2SO_4} \underset{\text{Ethyl borate}}{B(OC_2H_5)_3} + 3H_2O$$

ILLUSTRATION 6.20

Give reasons for the following:

a. Aluminium wire is used in transmission cables.
b. Aluminium utensils should not be used to store drinking water for long time.
c. A mixture of Al pieces and NaOH is used to open the drain.
d. Aluminium alloys are used to make aircraft bodies.

Sol.

a. Aluminium wire is used in transmission cables because of the following reasons:
   i. It is a good conductor of electricity.
   ii. It is not affected by atmosphere.
b. Aluminium is slowly attacked by water and dissolved O_2 to form Al_2O_3 on the surface. A very small amount of Al_2O_3 may get dissolved to form Al^{3+} ions. Since Al^{3+} ions are injurious to health, drinking water should not be stored in aluminium vessels.
c. NaOH reacts with Al to evolve hydrogen.

   $$2Al + 2NaOH \longrightarrow 2NaAlO_2 + H_2\uparrow$$

   This evolved hydrogen helps in opening the drain.
d. Aluminium alloys are light, tough and corrosion resistant. Hence, aluminium alloys are used to make aircraft bodies.

ILLUSTRATION 6.21

What happens when:

a. Borax is heated strongly.
b. Water is added to aluminium nitride.
c. Dry chlorine gas is passed over hot mixture of aluminium and coke.
d. Water is added to aluminium carbide.
e. Alum is heated.
f. Aluminium is added to copper sulphate solution.
g. Aluminium reacts with HNO_3.
h. Excess of caustic soda is added to a solution of aluminium chloride.
i. Aluminium is heated with caustic soda solution.
j. A mixture of borax and cobalt oxide is heated.

Sol.

a. $$\underset{\text{Borax}}{Na_2B_4O_7\cdot 10H_2O} \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{Boric anhydride}}{B_2O_3} + \underset{\text{Sodium metaborate}}{2NaBO_2}$$

b. $$\underset{\text{Aluminium nitride}}{AlN} + 3H_2O \longrightarrow \underset{\text{Aluminium hydroxide}}{Al(OH)_3\downarrow} + \underset{\text{Ammonia}}{NH_3\uparrow}$$

c. $$Al_2O_3 + 3C + \underset{\text{Dry}}{3Cl_2} \longrightarrow \underset{\text{Aluminium chloride}}{2AlCl_3} + \underset{\text{Carbon monoxide}}{3CO}$$

d. $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3\downarrow + 3CH_4\uparrow$

Aluminium carbide — Aluminium hydroxide — Methane

e. $K_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O \xrightarrow{200^\circ C} K_2SO_4\,Al_2(SO_4)_3 + 24H_2O$

$$K_2SO_4\cdot Al_2(SO_4)_3 \xrightarrow{\text{Red heat}} \underbrace{K_2SO_4 + Al_2O_3}_{\text{Burnt alum}} + 3SO_3\uparrow$$

Alum melts and loses water of crystallisation up to 200°C and a white porous mass is obtained on red heat. This white mass is known as *burnt alum*.

f. Aluminium being more electropositive than copper, displaces copper from copper sulphate solution.

$2Al_{(s)} + 3\,CuSO_{4(aq)} \longrightarrow Al_2(SO_4)_{3(aq)} + 3Cu_{(s)}$

g. HNO_3 whether concentrated or dilute hardly affects Al as aluminium is rendered passive due to formation of thin layer of Al_2O_3 on the surface of the metal.

h. $AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaCl$

i. $2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2\uparrow$

Sodium metaaluminate

j. $Na_2B_4O_7\cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$

$Na_2B_4O_7 \xrightarrow{\text{Red heat}} 2NaBO_2 + B_2O_3$

$CoO + B_2O_3 \longrightarrow Co(BO_2)_2$

Cobalt metaborate.

ILLUSTRATION 6.22

Starting from borax, how would you obtain:

a. Boric acid
b. Boron trioxide
c. Boron
d. Boron nitride
e. Boron trichloride

Sol.

a. By the acidification of borax,

$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$

b. By the acidification of borax,

$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$

Boric acid

followed by strong heating of boric acid,

$2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$

Boron oxide

c. By the acidification of borax,

$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$

followed by strong heating of boric acid,

$2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$

Boron oxide

and then reduction of boron oxide by strong electro-positive metal, Mg.

$B_2O_3 + Mg \longrightarrow MgO + B$

d. $Na_2B_4O_7 + NH_4Cl \longrightarrow 2BN + B_2O_3 + 2NaCl + 4H_2O$

Boron nitride

e. $B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO$

ILLUSTRATION 6.23

A mixture of boron trichloride and hydrogen is subjected to silent electric discharge to form (A) and HCl. (A) is mixed with ammonia and heated to 200°C to from (B). Identify (A) and (B).

Sol. $BCl_3 + H_2 \xrightarrow{\text{Silent electric discharge}} (A) + HCl$

$(A) + NH_3 \xrightarrow{200^\circ C} (B)$

$2\,BCl_3 + 6H_2 \xrightarrow{\text{Silent electric discharge}} \underset{(A)}{B_2H_6} + 6HCl$

$3B_2H_6 + 6NH_3 \xrightarrow{200^\circ C} \underset{(B)}{2B_3N_3H_6} + 12H_2$

(A) is diborane and (B) is borazine.

CONCEPT APPLICATION EXERCISE 6.1

1. Why boron does not exist as B^{3+} ion in solution or in compound?
2. The +1 oxidation state is more stable than +3 oxidation state for thallium. Give reason.
3. Aluminium chloride exists as dimer. Give reason.
4. Why boron halides do not exist as a dimer, while $AlCl_3$ exists as Al_2Cl_6 ?
5. Give reason for the following :
   a. In(III) is more stable than In(I) in aqueous solution.
   b. $InCl_3$ undergoes disproportionation but InCl does not.
   c. Unlike $In^{\oplus}$, $Tl^{\oplus}$ is more stable with respect to disproportionation.
   d. $Ga^{\oplus}$ undergoes disproportionation reactions.
6. Why boron and aluminium tend to form covalent compounds?
7. Molten aluminium bromide is a poor conductor of electricity. Give reason.
8. Why B–X bond distance in BX_3 is shorter than theoretically expected value?
9. Boric acid can be titrated against sodium hydroxide using phenolphthalein as an indicator only in the presence of polyhydroxy compounds like glycol, glycerol etc. Give reason.
10. Which one is more soluble in diethyl ether: anhydrous $AlCl_3$ or hydrated $AlCl_3$? Explain in terms of bonding.
11. How is boron abtained from borax? Give the chemical reactions involved. Draw the structure of B_2H_6 and give its reaction with HCl.

12. Unlike ordinary fire, thermite reaction cannot be stopped by pouring water. Explain.
13. Explain why BF_3 exist but BH_3 does not.
14. State with equations what happens when borax is heated on a platinum wire loop and to the resulting transparent mass, a minute amount of CuO is added and the mixture is again heated. (a) First in the oxidising flame and (b) Then in the reducing flame of a Bunsen burner?
15. What is inorganic benzene? Why is it so called? How will you get it from diborane?
16. AlF_3 is insoluble in anhydrous HF but dissolves on addition of NaF. AlF_3 precipitates out of the resulting solution when gaseous BF_3 is bubbled through. Give reasons.
17. What do you understand by:
    a. Ammonal
    b. Bentonite
    c. Rubies and Sapphire
    d. Lapis lazuli
    e. Emery paper

Solved Examples

Example 6.1

When an inorganic compound (X) having (3*c*, 2*e*) as well as (2*c*, 2*e*) bonds react with ammonia gas at a certain temperature and gives a compound (Y), which is isostructural with benzene. Compound (X) with ammonia at very high temperature gives (Z) also known as inorganic graphite. Identify (X), (Y) and (Z).

Sol.

$$\underset{\text{Inorganic compound}}{(X)} \xrightarrow[\Delta]{NH_3} \underset{\text{Isostructural with benzene}}{(Y)}$$

$$\underset{\text{Inorganic compound}}{(X)} \xrightarrow[\text{Very high temperature}]{NH_3} \underset{\text{Inorganic graphite}}{(Z)}$$

Inorganic graphite (Z) is boron nitride. Since diborane reacts with ammonia at very high temperature to give inorganic graphite (X) is diborane, B_2H_6. Diborane contains both (3*c*, 2*e*) and (2*c*, 2*e*) bonds.

$$B_2H_6 + NH_3 \longrightarrow \underset{\text{Borazine (Y)}}{B_3N_3H_6}$$

Borazine is isostructural with benzene, C_6H_6. Hence, (X) is diborane, B_2H_6; (Y) is borazine, $B_3N_3H_6$ and (Z) is boron nitride $(BN)_x$

Example 6.2

Boric acid on heating at 100°C, gives (X). (X) on heating at 160°C gives (Y) and (Y) on heating at red hot gives (Z). Identify (X), (Y) and (Z).

Sol.

$$H_3BO_3 \xrightarrow{100°C} \underset{\text{Metaboric acid (X)}}{HBO_2} + H_2O$$

$$4HBO_2 \xrightarrow{160°C} \underset{\text{Tetraboric acid (Y)}}{H_2B_4O_7} + H_2O$$

$$H_2B_4O_7 \xrightarrow{\text{Red hot}} \underset{(Z)}{B_2O_3} + H_2O$$

Hence, (X) is metaboric acid, HBO_2; (Y) is tetraboric acid, $H_2B_4O_7$ and (Z) is boric oxide, B_2O_3.

Example 6.3

Amorphous boron is extracted from borax by the following steps:

$$\text{Borax} \xrightarrow{(A)} H_3BO_3 \xrightarrow{\text{Heat}} B_2O_3 \xrightarrow{(B)} \text{Boron}$$

(A) and (B) are

a. H_2SO_4, Al
b. HCl, Carbon
c. H_2SO_4, Mg
d. HCl, Fe

Sol. Boric acid, H_3BO_3, is formed by acidification of hot concentrated solution of borax by hot and conc solution of H_2SO_4.

$$Na_2B_4O_7 + 5H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

$$\left\{\begin{array}{l} H_3BO_3 \xrightarrow{\Delta} B_2O_3 + H_2O \\ B_2O_3 + 3Mg \longrightarrow 2B + 3MgO \end{array}\right\}$$

B_2O_3 is reduced to B by strong electropositive element only. Hence (A) is H_2SO_4 and (B) is Mg.

Therefore, option (c) is correct.

Example 6.4

A certain salt (X) gives the following tests:

a. Its aqueous solution is alkaline to litmus.
b. On strong heating, it swells to give a glassy bead.
c. When conc H_2SO_4 is added to a hot concentrated solution of (X), white crystals of a weak acid separates out. Identify (X) and write down the chemical equations for reactions at steps a, b and c.

Sol. As given, (X) on strong heating, swells to give a glassy bead, (X) is borax, $Na_2B_4O_7 \cdot 10H_2O$

a. $$Na_2B_4O_7 + 7H_2O \rightleftharpoons \underset{\text{Strong base}}{2NaOH} + \underset{\text{Weak acid}}{4H_3BO_3}$$

In aqueous solution, borax hydrolyse to give a strong base, NaOH, and a weak acid, H_3BO_3. Hence, the solution will be alkaline to litmus.

b. $$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \xrightarrow{\text{Strong heating}} \underset{\text{Sodium metaborate}}{NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$$

B_2O_3 forms glassy bead.

c. $$\underset{\text{Hot and conc}}{Na_2B_4O_7} + \underset{\text{Conc}}{H_2SO_4} + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3\downarrow$$

Sodium sulphate, Na_2SO_4, is soluble in water and white crystals of boric acid, H_3BO_3 (weak acid), separates out.

EXAMPLE 6.5

A white crystalline compound (X) swells upon heating and gives violet-coloured flame. Its aqueous solution gives the following reactions:

a. A white precipitate is formed, with $BaCl_2$ in presence of HCl.

b. When treated with excess of NH_4OH, it gives white gelatinous precipitate. The white precipitate dissolves in NaOH and reappears on boiling with concentrated solution of NH_4Cl.

c. It gives yellow precipitate with cobaltinitrite solution.

Identify (X) and explain the reactions at steps a, b and c.

Sol. The given compound (X) swells on heating due to evolution of water molecules. It also, gives violet coloured flame due to the presence of potassium salt.

The given compound (X) is potash alum, $K_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$ which gives the following reactions:

a. With $BaCl_2$ in presence of HCl, a white precipitate is formed. The aqueous solution contains SO_4^{2-} ions, which react with Ba^{2+} ions to give white precipitate of $BaSO_4$, which is insoluble in conc HCl.

$$Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow \underset{\text{White ppt.}}{BaSO_4\downarrow}$$

b. With excess of NH_4OH, white geletinous precipitate

$$Al_2(SO_4)_3 + 6NH_4OH \longrightarrow \underset{\text{White gelatinous precipitate}}{2\,Al(OH)_3\downarrow} + 3(NH_4)_2\,SO_4$$

of aluminium hydroxide, $Al(OH)_3$, is formed. $Al(OH)_3$ dissolves in NaOH forming sodium meta-aluminate.

$$Al(OH)_3 + NaOH \longrightarrow \underset{\text{Sodium meta-aluminate (soluble)}}{NaAlO_2} + 2H_2O$$

The white precipitate reappears when the above solution is boiled with concentrated solution of NH_4Cl, due to the formation of white precipitate of aluminium hydroxide, $Al(OH)_3$.

$$NaAlO_2 + NH_4Cl + H_2O \longrightarrow Al(OH)_3\downarrow + NH_3 + NaCl$$

c. Potassium salts give yellow precipitate of potassium cobaltinitrite with cobaltinitrite solution.

$$2K_2SO_4 + Na_4[Co(NO_2)_6] \longrightarrow \underset{\text{Yellow ppt}}{K_4[Co(NO_2)_6]\downarrow} + 2Na_2SO_4$$

or

$$4K^{\oplus} + [Co(NO_2)_6]^{4-} \longrightarrow \underset{\text{Potassium cobaltinitrite}}{K_4[Co(NO_2)_6]\downarrow}$$

EXAMPLE 6.6

The metallic salt (XY) is soluble in water.

a. When the aqueous solution of (XY) is treated with NaOH solution, a white precipitate (A) is formed. In excess of NaOH solution, white precipitate (A) dissolves to form a compound (B). When this solution is boiled with solid NH_4Cl, a precipitate of compound (C) is formed.

b. An aqueous solution on treatment with $BaCl_2$ solution gives a white precipitate (D) which is insoluble in conc HCl.

c. The metallic salt (XY) forms a double salt (E) with potassium sulphate.

Identify (XY), (A), (B), (C), (D) and (E).

Sol.

a. $$(XY)_{(aq)} \xrightarrow{\text{NaOH soln}} \text{White ppt. (A)} \xrightarrow{\text{Excess NaOH}} \underset{\text{Soluble}}{(B)} \xrightarrow[\Delta]{NH_4Cl} \underset{\text{White ppt.}}{(C)}$$

(X) is Al^{3+} ion.

$$Al^{3+}_{(aq)} + 3NaOH_{(aq)} \longrightarrow \underset{\substack{\text{White ppt.}\\ \text{(A)}}}{Al(OH)_3\downarrow} + 3Na^{\oplus}$$

$$Al(OH)_3 + \underset{\text{Excess}}{NaOH_{(aq)}} \longrightarrow \underset{\substack{\text{(B)}\\ \text{Sodium meta-aluminate}}}{NaAlO_2} + 2H_2O$$

$$NaAlO_2 + NH_4Cl + H_2O \xrightarrow{\text{Heat}} \underset{\substack{\text{(C)}\\ \text{Aluminium hydroxide}}}{Al(OH)_3\downarrow} + NaCl + NH_3$$

The metallic salt (XY) on treatment with NaOH solution, gives a white precipitate of aluminium hydroxide. $Al(OH)_3{\cdot}Al(OH)_3$ dissolves in excess of NaOH solution forming sodium metaaluminate, $NaAlO_2{\cdot}NaAlO_2$ on boiling with NH_4Cl solution gives while precipitate of aluminium hydroxide, $Al(OH)_3$.

b. $$(XY)_{(aq)} \xrightarrow{BaCl_2\text{ solution}} \underset{\text{white ppt.}}{(D)} \xrightarrow{\text{conc HCl}} \underset{\text{Insoluble}}{(D)}$$

(Y) is SO_4^{2-} ion.

$$SO_4^{2-}{}_{(aq)} + Ba^{2+}_{(aq)} \longrightarrow \underset{\text{While ppt.}}{BaSO_4\downarrow}$$

(D) is barium sulphate, $BaSO_4$, which is insoluble in conc HCl.

Hence, the salt (XY) is $Al_2(SO_4)_3$, aluminium sulphate.

c. The double salt (E) formed by (XY) with potassium sulphate is $K_2SO_4{\cdot}Al_2(SO_4)_3\cdot 24H_2O$ i.e. potash alum.

Hence, (XY) is $Al_2(SO_4)_3$; (A) is $Al(OH)_3$; (B) is $NaAlO_2$; (C) is $Al(OH)_3$; (D) is $BaSO_4$ and (E) is $K_2SO_4{\cdot}Al_2(SO_4)_3$ $\cdot 24H_2O$.

EXAMPLE 6.7

An inorganic compound (X) shows the following reactions:

a. It is white solid, exists as dimer and fumes in moist air.

b. It sublimes at 180°C and forms monomer on heating to 400°C.

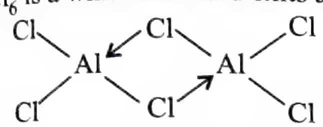
c. Its aqueous solution turns blue litmus red and gives a white precipitate with $AgNO_3$ solution which is soluble in excess of NH_4OH.

d. Addition of NaOH to the solution of (A) gives a white gelatinous precipitate which is, however, soluble in excess of NaOH.

Identify the compound (A).

Sol. (A) is Al_2Cl_6.

a. Al_2Cl_6 is a white solid and exits as dimer.



Al_2Cl_6 fumes in moist air due to evolution of HCl gas.

$$Al_2Cl_6 + 6H_2O \longrightarrow 2Al(OH)_3 + 6HCl\uparrow$$

b. $$Al_2Cl_{6(s)} \xrightarrow{180°C} Al_2Cl_{6(g)} \xrightarrow{400°C} 2AlCl_3$$

c. Aqueous solution of Al_2Cl_6 contains hydrated aluminium chloride, Al_2Cl_6, which is ionic in nature.

$$Al_2Cl_6 + 6H_2O \longrightarrow Al_2Cl_6{\cdot}6H_2O \text{ or } 2AlCl_3{\cdot}6H_2O$$

$$AlCl_{3(aq)} \rightleftharpoons Al^{3+}_{(aq)} + 3Cl^{\ominus}_{(aq)}$$

Since the above solution is acidic, it turns blue litmus red.

$$AlCl_3 + 3H_2O \longrightarrow \underset{\text{Weak base}}{Al(OH)_3} + \underset{\text{Strong acid}}{3HCl}$$

On addition of $AgNO_3$ solution in aqueous solution of aluminium chloride, white precipitate of AgCl is formed.

$$Cl^{\ominus}_{(aq)} + Ag^{\oplus}_{(aq)} \longrightarrow \underset{\text{(White ppt.)}}{AgCl\downarrow}$$

AgCl is soluble in excess of NH_4OH due to the formation of soluble complex, $[Ag(NH_3)_2]Cl$.

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{Diamminesilver(I) chloride}}{[Ag(NH_3)_2]Cl} + 2\overset{\ominus}{O}H$$

d. Aqueous solution of (A) + NaOH $\longrightarrow$ White gelatinous ppt.

$\downarrow$ Excess NaOH

White ppt. dissolves

$$Al^{3+} + NaOH \longrightarrow \underset{\text{White ppt.}}{Al(OH)_3\downarrow} + Na^{\oplus}$$

$$Al(OH)_3 + \underset{\text{Excess}}{NaOH} \longrightarrow \underset{\text{Sodium metaaluminate}}{NaAlO_2} + 2H_2O$$

Due to the formation of $Al(OH)_3$ intially, white gela-tionous precipitate is obtained, which dissolves in excess of NaOH due to the formation of sodium meta- aluminate.

EXAMPLE 6.8

Compound (X) on reduction with $LiAlH_4$ gives a hydride (Y) containing 21.72% hydrogen along with other products. The compound (Y) reacts with air explosively resulting in formation of boron trioxide. Identify (X) and (Y). Give balanced reactions involved in the formation of (Y) and its reaction with air. Give the structure of (Y).

Sol. $$(X) + LiAlH_4 \xrightarrow{\text{Reduction}} \underset{\text{Hydride, 2.72 \% H}}{(Y)} + \text{Other products}$$

$$(Y) + \text{Air} \xrightarrow[\text{reaction}]{\text{Explosive}} B_2O_3$$

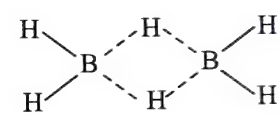
Determination of the molecular formula and structure of compound (Y): Since the hydride (Y) reacts with air forming boron trioxide, therefore (Y) must be hydride of boron.

Given % H = 21.72 %

$\therefore$ % B = (100 – 21.72)% = 78.28%

$$B : H = \frac{78.28}{11} : \frac{21.72}{1} = 1:3$$

Hence, B and H are present in the ratio 1:3. Simplest boron hydride corresponding to this ratio is B_2H_6. Hence, (Y) is diborane B_2H_6.



Determination of (X): Since B_2H_6 is formed by the reduction of (X) with $LiAlH_4$, therefore (X) is either BF_3 or BCl_3

$$\underset{(X)}{4BCl_3} + 3LiAlH_4 \longrightarrow \underset{(Y)}{2B_2H_6} + 3LiAlF_4$$

The equation representing the reaction of (Y) with oxygen is

$$B_2H_6 \longrightarrow \underset{\text{Boron trioxide}}{B_2O_3} + 3H_2O$$

Hence, (X) is BCl_3 and (Y) is B_2H_6.

EXAMPLE 6.9

An inorganic Lewis acid (X) shows the following reactions:

a. It fumes in moist air.

b. The intensity of fumes increases when a rod dipped in NH_4OH is brought near it .

c. To an aqueous solution of (X), addition of NH_4Cl and NH_4OH gives a precipitate which dissolves in NaOH solution.

d. An acidic solution of (X) does not give a precipitate with H_2S.

Identify (X) and give chemical reactions for (a) to (d).

Sol. (X) is Lewis acid and fumes in moist air, it may be anhydrous $AlCl_3$.

a. $$AlCl_3 + \underset{\text{(Air)}}{H_2O} \longrightarrow Al(OH)_3\downarrow + \underset{\text{(Fumes)}}{3HCl}$$

$AlCl_3$ fumes in moist air due to evolution of HCl gas.

b. When a rod dipped in NH_4OH is brought near it, the intensity of fumes increases due to the formation of ammonium chloride NH_4Cl.

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$

c. $$AlCl_{3(aq)} + 3NH_4OH \xrightarrow{NH_4Cl} Al(OH)_3\downarrow + 3NH_4Cl$$

$$Al(OH)_3 + NaOH \longrightarrow \underset{\substack{\text{(Soluble)}\\ \text{Sodium}\\ \text{metaaluminate}}}{NaAlO_2} + 2H_2O$$

An aqueous solution of (X) i.e. $AlCl_3$ gives a white precipitate of aluminium hydroxide $Al(OH)_3$, on addition of NH_4Cl and NH_4OH. $Al(OH)_3$ dissolves is NaOH solution due to the formation of sodium meta-aluminate, $NaAlO_2$.

d. No precipitate is formed when H_2S is passed through acidic solution of (X), i.e. $AlCl_3$.

EXAMPLE 6.10

a. On boiling a mineral (A) with $NaCO_3$ solution, a white precipitate (B) is formed.

b. The precipitate is filtered and the filtrate contains two compounds (C) and (D). The compound (C) is removed by crystallisation and when CO_2 is passed through the mother liquor left, (D) changes to (C).

c. On strongly heating (C), two compounds (D) and (E) are formed.

d. (E) on heating with cobalt oxide provides blue-coloured substance (F).

Identify (A) to (F) and give chemical reactions for (a) to (d).

Sol.

a. The mineral (A) is colemanite, $Ca_2B_6O_{11}\cdot 5H_2O$

$$\underset{(A)}{Ca_2B_6O_{11}\cdot 5H_2O} + 2Na_2CO_{3(aq)} \xrightarrow{\text{Boiled}}$$

$$2CaCO_3\downarrow + \underbrace{\underset{(C)}{Na_2B_4O_{7(aq)}} + \underset{(D)}{2NaBO_{2(aq)}}}$$

(B), i.e. white ppt. is of calcium carbonate.

b. The filterate formed in step (a) contains borax $Na_2B_4O_7$ (C) and sodium metaborate, $NaBO_2$ (D).

On crystallisation, borax gets separated out in the form of white crystals. Filterate now consists of $NaBO_2$ only. On passing CO_2 though the filterate, sodium metaborate $NaBO_2$ (D) reacts to form borax $Na_2B_4O_7$, i.e. (C).

$$\underset{(D)}{NaBO_2} + CO_2 \longrightarrow \underset{(C)}{Na_2B_4O_7} + Na_2CO_3$$

c. On strongly heating (C), sodium metaborate (D) and boron tioxide (E) are formed.

$$Na_2B_4O_7\cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \xrightarrow{\Delta} \underset{(D)}{2NaBO_2} + \underset{\substack{(E)\\ \text{Boron trioxide}}}{B_2O_3}$$

d. On heating (E) with cobalt oxide (CoO), blue-coloured cobalt metaborate, $Co(BO_2)_2$ (F) is formed.

$$B_2O_3 + CoO \longrightarrow \underset{\substack{\text{Cobalt metaborate}\\ \text{(blue coloured)}}}{Co(BO_2)_2}$$

Hence, (A) is $Ca_2B_6O_{11}\cdot 5H_2O$; (B) is $CaCO_3$; (C) is $Na_2B_4O_7\cdot 10H_2O$; (D) is $NaBO_2$ and (E) is $Co(BO_2)_2$.

EXAMPLE 6.11

Identify (A), (B), (C) and (D) in the following:

$$\text{Metal (A)} + N_2 \xrightarrow{\Delta} (B) \xrightarrow{H_2O} \underset{\text{White ppt.}}{(C)}\downarrow + (D)_{(g)}$$

White precipitate (C) dissolves is NaOH solution while the gas (D) gives white fumes with HCl.

Sol. Metal (A) on heating with nitrogen, N_2, gas gives (B) which on hydrolysis gives a white ppt. (C) and a gas (D). Since precipitate (C) dissolves in NaOH solution, metal (A) must be aluminium, Al. As the gas (D) gives white fumes with HCl, (D) is ammonia (NH_3).

$$\underset{(A)}{2Al} + N_2 \xrightarrow{\Delta} \underset{\substack{(B)\\ \text{Aluminium nitride}}}{2AlN}$$

$$\underset{(B)}{AlN} + H_2O \longrightarrow \underset{\substack{(C)\\ \text{Alm uninium}\\ \text{hydroxide}\\ \text{(white ppt.)}}}{Al(OH)_3\downarrow} + \underset{\substack{(D)\\ \text{Ammonia}}}{NH_3\uparrow_{(g)}}$$

$$Al(OH)_3 + NaOH_{(aq)} \longrightarrow \underset{\substack{\text{Sodium}\\ \text{metaaluminate}\\ \text{(soluble)}}}{NaAlO_2} + 2H_2O$$

$$\underset{(D)}{NH_3} + HCl \longrightarrow \underset{\text{(White fumes)}}{NH_4Cl}$$

Hence (A) is Al; (B) is AlN; (C) is $Al(OH)_3$ and (D) is NH_3.

EXAMPLE 6.12

A colourless mixture of two salts (A) and (B) (excess) is soluble in H_2O. (A) turns blue litmus red and (B) turns red litmus blue. (A) gives white precipitate with (B), which dissolves in excess of (B) forming (C). (A) when placed in atmosphere gives fumes and can form dimer. (A) gives white precipitate with NH_4Cl and NH_4OH which is soluble in (B). Identify (A), (B) and (C). Explain reactions.

Sol. (A) gives white ppt. with NH_4Cl and NH_4OH. Hence, (A) is Al^{3+} and, white precipitate is of $Al(OH)_3$.

$Al(OH)_3$ is soluble in (B), therefore, (B) is NaOH and (C) is $NaAlO_2$ (sodium meta-aluminate).

(A) forms dimer which indicates (A) is electron-deficient compound that is possible in case of $AlCl_3$.

(A) is thus $AlCl_3$ (acidic due to hydrolysis, turns blue litmus red).

(B) is NaOH (alkaline, turns red litmus blue).

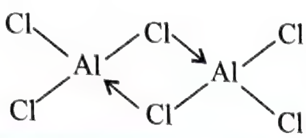
$$\underset{(A)}{AlCl_3} + \underset{(B)}{3NaOH} \longrightarrow \underset{\text{White ppt.}}{Al(OH)_3} + 3NaCl$$

$$Al(OH)_3 + \underset{(\text{Excess})}{NaOH} \longrightarrow \underset{\substack{\text{Soluble}\\(C)}}{NaAlO_2} + H_2O$$

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl\uparrow(\text{Fumes})$$

$$AlCl_3 + 3NH_4OH \xrightarrow{NH_4Cl} Al(OH)_3 + 3NH_4Cl$$

$$2AlCl_3 \longrightarrow Al_2Cl_6$$



EXAMPLE 6.13

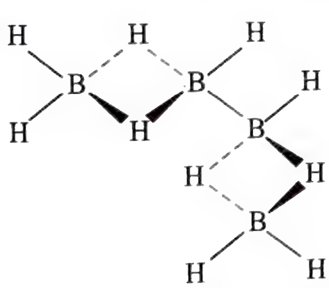
$B_{10}C_2H_{12}$ is isostructural and isoelectronic with what borane ion, $B_xH_y^{z-}$?

Sol. $B_{12}H_{12}^{2-}$. Each of the boron atoms has one fewer electron than a carbon atom. To keep the total number of electrons the same in $B_{10}C_2H_{12}$ and the boron hydride ion, the replacement of two carbon atoms with boron atoms must be accompanied by addition of two extra electrons.

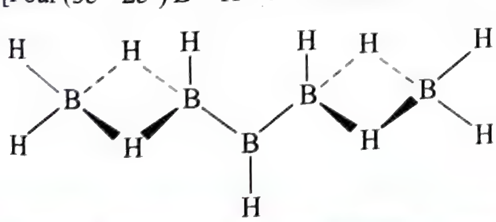
EXAMPLE 6.14

Draw possible structures of B_4H_{10} and B_5H_{11} molecules, showing the existence of $(3c, 2e)$ bridge bonds.

Sol. (a) B_4H_{10} [Four $(3c - 2e^-)$ B····H····B bonds and one B····B) bond,



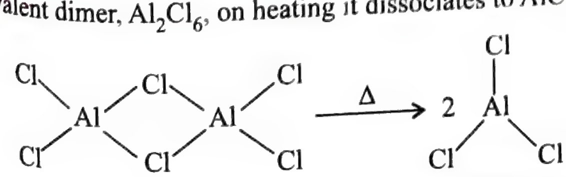
(b) B_5H_{11} [Four $(3c - 2e^-)$ B····H····B bonds and two (B····B) bond,



EXAMPLE 6.15

How the electrical conductivity of Al_2Cl_6 changes on heating?

Sol. $AlCl_3$ is ionic in the solid state, hence conducting but melts to covalent dimer, Al_2Cl_6, on heating it dissociates to $AlCl_3$.



(Al_2Cl_6) (Non conducting) $\qquad$ $(AlCl_3)$ (Conducting)

EXAMPLE 6.16

Complete the following:

a.

$$\text{Compound (W)} + 3NH_4Cl \xrightarrow{140°C} B_3N_3H_3Cl_3(X) \xrightarrow{NaBH_4} \text{Compound (Y)} [B_3N_3H_6]$$

$$B_3N_3H_3Cl_3(X) \xrightarrow{CH_3MgBr} \text{Compound (Z)} [B_3N_3H_3(CH_3)_3]$$

b.

$$\text{Element (E)} \xrightarrow[\text{Air}]{\Delta} F \xrightarrow[\text{in electric furnance}]{+\text{ Carbon}} G$$

$$F \xrightarrow{\Delta \text{ in } N_2} H$$

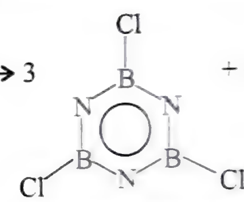
$$H \xrightarrow[H_2O]{\text{Steam}} \underset{\text{Boric acid}}{H_3BO_3} + \underset{(I)}{\text{Colourless gas}}$$

$$(I) \xrightarrow{HCl} \text{white fumes}$$

Sol.

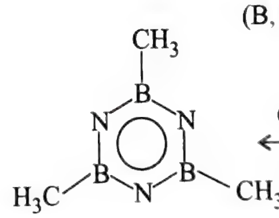
a. Since the compound of boron is obtained, so compound (X) is BCl_3. Reactions are:

$$\underset{(W)}{9BCl_3} + 9NH_4Cl \xrightarrow{140°C} 3\,[\text{structure}] + 27\,HCl$$

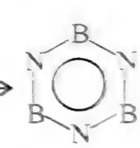


(B, B, B-Trichloroborazine (X))

$$(X) \xrightarrow{CH_3MgBr} (Z) \qquad (X) \xrightarrow{NaBH_4} (Y)$$



(B, B, B-Trimethyl borazine) (Z) $[B_3N_3H_3(CH_3)_3]$



(Borazine) (Y) $(B_3N_3H_6)$

b. Since the end product is boric acid (H_3BO_3) hence the element E, must be boron (B).

$$\underset{(\text{Element E})}{B} \xrightarrow[\text{Air}]{\Delta} \underset{(F)}{B_2O_3} + C \xrightarrow[\text{furnance}]{\text{Electric}} \underset{\substack{(\text{Boron Carbide})\\(G)}}{B_4C_3}$$

$$(F) \xrightarrow{N_2} \underset{\substack{(H)\\\text{Boron nitride}}}{BN} \xrightarrow[H_2O]{\text{Steam}} \underset{\text{Boric acid}}{H_3BO_3} + \underset{(I)}{NH_{3(g)}}$$

$$NH_{3(g)} \xrightarrow{HCl} \underset{\text{White fumes}}{NH_4Cl}$$

Reactions are:

i. $\underset{(E)}{4B} + 3O_2 \longrightarrow \underset{(F)}{2B_2O_3}$

ii. $B_2O_3 + N_{2(g)} \longrightarrow 2BN + 3/2\ O_{2(g)}$
(F) (H)

iii. $2BN + 3H_2O \longrightarrow B_2O_3 + 2NH_3$

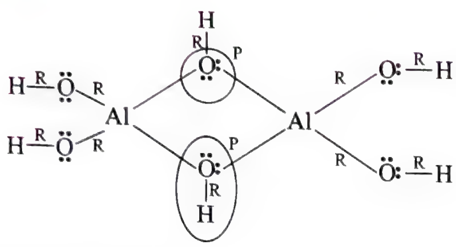
$B_2O_3 + H_2O \longrightarrow HBO_2$

$HBO_2 + H_2O \longrightarrow H_3BO_3$(Boric acid)

EXAMPLE 6.17

Considering $Al_2(OH)_6$ compound, calculate the value of $\dfrac{R}{P+Q}$.
where P = Total number of $(3C - 4e^-)$ bond,
Q = Total number of $(3C - 2e^-)$ bond
R = Total number of $(2C - 2e^-)$ bond.

Sol. (5)



$P = (3C - 4e^-)$ bond $= 2$
$Q = (3C - 2e^-)$ bond $= 0$
$R = (2C - 2e^-)$ bond $= 10$

$$\therefore \frac{R}{P+Q} = \frac{10}{2+0} = 5$$

EXAMPLE 6.18

How many boron atoms in anionic part of borax occurs back bonding?

Sol. (2) Borax $= 2Na^{\oplus}\ [B_4O_5(OH)_4]^{2-} \cdot 8H_2O$

Refer to Structure of Boron Section 6.11.1

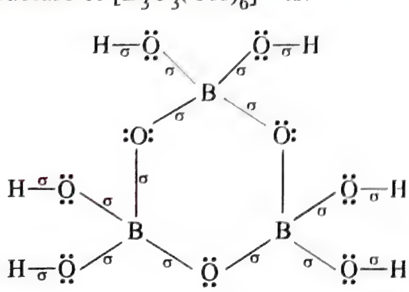
sp^2 hybridized B-atoms only participate in $(p\pi\text{-}p\pi)$ back bonding.

EXAMPLE 6.19

Consider $[B_3O_3(OH)_6]^{3-}$ molecular ion.
If X = Total number of σ-bonds
Y = Total number of lone pairs.

Calculate the value of $\dfrac{X+Y}{9}$.

Sol. (4) Structure of $[B_3O_3(OH)_6]^{3-}$ is:



$\therefore X = 18, Y = 18$

$$\therefore \frac{X+Y}{9} = \frac{36}{9} = 4$$

EXAMPLE 6.20

Identify A to G

(i) $\underset{(A)}{B_2O_3} + 3C + 3Cl_2 \longrightarrow (B) + C(gas)$
$(B) \xrightarrow{3H_2O} (D)$

(ii) $(E) \xrightarrow{3H_2O} (D) + 3HCl$

(iii) $B + LiAlH_4 \longrightarrow (F) + 3LiCl + 3AlH_4$
$(F) \xrightarrow{2NaH} (G)$
$(F) \xrightarrow{6H_2O} (D) + 6H_2$ (Gas)

Sol.

(i) $\underset{(A)}{B_2O_3} + 3C + Cl_2 \longrightarrow \underset{(B)}{2BCl_3} + \underset{(C)}{3\ CO}$
$2BCl_3 \xrightarrow{3H_2O} H_3BO_3$

(ii) $\underset{(E)}{BN} + 3H_2O \longrightarrow \underset{(D)}{H_3BO_3} + 3HCl$

(iii) $\underset{(B)}{4BCl_3} + 3LiAlH_4 \longrightarrow \underset{(F)}{2B_2H_6} + 3LiCl + 3AlCl_3$
$2B_2H_6 \xrightarrow{2NaH} \underset{(G)}{2NaBH_4}$
$2B_2H_6 \xrightarrow{6H_2O} \underset{(D)}{2H_3BO_3} + 6H_2$

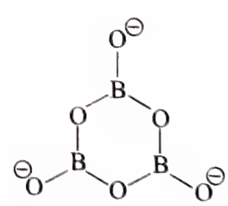
EXAMPLE 6.21

Find the geometry (planar or non-planar) of the following molecules.

a. $B_3O_6^{3-}$
b. Fe_2Cl_6
c. Trimer of FCN
d. Borazone
e. Borazole
f. $(BN)_x$
g. Graphite.

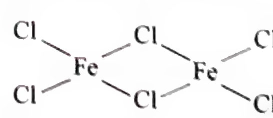
Sol.

a. $B_3O_6^{-3}$:



(Planar)

b. Fe_2Cl_6:



(Non-planar)

c. $(FCN)_3$:

(Planar)

d. Borazone: It is crystalline form of BN (boron nitride) which has diamond like structure (sp^3, hybridized, non-planar)
e. Borazole: Inorganic benzene $B_3N_3H_6$ (planar)
f. $(BN)_x$: Graphite like structure (planar)
g. Graphite: Planar

EXAMPLE 6.22

a. How borax is converted into crystalline boron.

b. What happens when salicylic acid reacts with aqueous solution of boric acid.

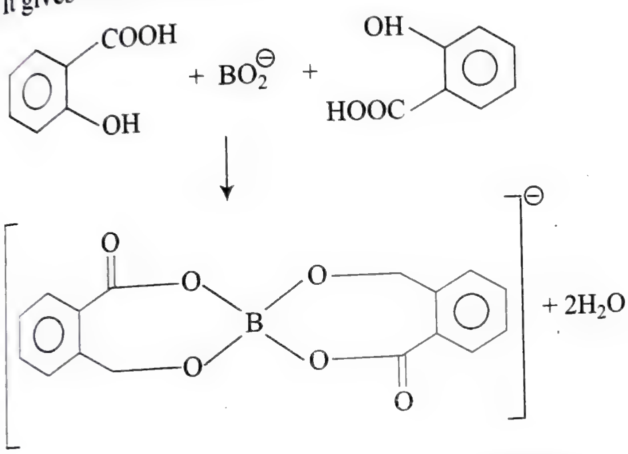
Sol.

a. $Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3 \xrightarrow{\Delta}$

$6H_2O + 2B_2O_3 \xrightarrow{6\,Mg} 2B + 6MgO$ (crystalline boron)

b. (i) $B(OH)_3 \xrightleftharpoons{H_2O} [B(OH)_4]^{\ominus} + H^{\oplus} \rightleftharpoons BO_2^{\ominus} + 2H_2O$

(ii) It gives 4-coordinated complex, and optically active



Optically resolvable due to asymmetric structure

EXAMPLE 6.23

In borax,

If P = Number of sp^3 hybridized B atoms.

Q = Number of B–O–B bonds.

R = Number of B–B bonds.

S = Number of B atoms participate in $(p\pi - p\pi)$ multiple bond.

T = Number of H_2O molecules as water of crystallization.

Calculate the value of $\dfrac{P+Q+T}{R+S}$.

Sol. **(7.5)** Refer to the structure of borax (see. 6.11)

$Na_2[B_4O_5(OH)_4] \cdot 8H_2O$.

$P = 2, Q = 5, R = 0, S = 2, T = 8$.

$$\therefore \frac{P+Q+T}{R+S} = \frac{2+5+8}{0+2} = \frac{15}{2} = 7.5$$

Exercises

Single Correct Answer Type

Physical and chemical properties

1. Boron behaves as:
   (1) Non-metal (2) Metal
   (3) Metalloid (4) Transition metal
2. Which of the following is not a mineral of boron?
   (1) Colemanite (2) Kernite
   (3) Boric anhydride (4) Borax
3. Which of the following compounds is formed in borax bead test?
   (1) Metaborate (2) Tetraborate
   (3) Double oxide (4) Orthoborate
4. Which of the following minerals does not contain aluminium?
   (1) Cryolite (2) Mica
   (3) Feldspar (4) Flourspar
5. The stability of +1 oxidation state increases in the sequence:
   (1) $Tl < In < Ga < Al$ (2) $In < Tl < Ga < Al$.
   (3) $Ga < In < Al < Tl$ (4) $Al < Ga < In < Tl$
6. Boron does not form B^{3+} ion, due to
   (1) Energy required to form B^{3+} ion is very high which will not be compensated by lattice enthalpies or hydration enthalpies of such ion.
   (2) Boron is a non-metal.
   (3) Boron is a metalloid.
   (4) None of the above.
7. When aluminium is heated in atomoshere of nitrogen it forms:
   (1) AlN (2) Al_2N
   (3) Al_3N (4) Al_2N_3
8. Which one of the following is more abundant in the earth's crust?
   (1) B (2) Al
   (3) Ga (4) In
9. The liquified metal expanding on solidification is
   (1) Al (2) Ga
   (3) Zn (4) Cu
10. Which is used in high temperature thermometry?
    (1) Na (2) Ti
    (3) Ga (4) Hg
11. The colour of ferric metaborate is
    (1) Yellow (2) Blue
    (3) Green (4) Grey
12. Aluminium is more reactive than iron. But aluminium is less easily corroded than iron because
    (1) Iron forms mono and divalent ions.
    (2) Iron undergoes reaction easily with water.
    (3) Oxygen forms a protective oxide layer on aluminium.
    (4) Aluminium is a noble metal.
13. Boron has an extremely high melting point because of
    (1) Allotropy
    (2) Its ionic crystal structure
    (3) Strong van der Waals forces between its atoms
    (4) Strong binding forces in the covalent polymer.
14. Boron nitride is isoelectronic with
    (1) C_2 (2) B_2
    (3) N_2 (4) O_2
15. Which one of the following is hardest compound of boron?
    (1) Boron carbide (2) Boron nitride
    (3) Magnesium boride (4) Silicon boride
16. Which halides of the element of group 13 do not exist as dimer in the vapour state, the element is
    (1) Al (2) B
    (3) Ga (4) Tl
17. Which of the following exhibits inert pair effect?
    (1) B (2) Al
    (3) Tl (4) Sc
18. Silicon resembles B due to
    (1) Similar values of atomic radii
    (2) Similar values of EN
    (3) Similar values of IE
    (4) All of the above
19. Al salts on heating with Na_2CO_3 in charcoal cavity gives a white infusible residue. On moistening the same with a drop of cobalt nitrate, it changes to ________ due to the formation of cobalt meta-aluminate (Thenard's blue)
    (1) Brown (2) Yellow
    (3) Blue (4) Lemon
20. Thallium shows different oxidation states due to:
    (1) Inert pair effect (2) Amphoteric nature
    (3) Transition metal (4) High reactivity
21. Aluminium vessels should not be washed with materials containing washing soda because:
    (1) Washing soda reacts with aluminium to form soluble aluminate.
    (2) Washing soda is expensive.
    (3) Washing soda is easily decomposed.
    (4) Washing soda reacts with aluminium to form insoluble aluminium oxide.
22. B_2H_6 and B_4H_{10} respectively are examples of
    (1) Nido and arachno boranes
    (2) Nido and closo boranes
    (3) Closo and arachno boranes
    (4) Nido boranes

23. In the thermite process, iron oxide is reduced to molten iron by Al powder because
(1) The melting point of Fe is low
(2) The reaction is highly endothermic
(3) Larger amount of heat is liberated in the formation of Al_2O_3
(4) Al is an amphoteric element

24. Thalium (Tl) exhibits monovalency whereas Al exhibits trivalency. This is due to:
(1) The energy required to unpair outer *s*-electrons in Tl exceeds the energy involved in bond formation.
(2) Tl has only one electron in its outermost orbital.
(3) Al can use its vacant *d*-orbitals for the bond formation
(4) Tl is a non-metal.

25. Which of the following atom would likely form a cation.
(1) B (2) Si
(3) Al (4) C

26. Select the incorrect statement
(1) HNO_3 can be stored in aluminium vessels.
(2) Al is more reactive than Fe
(3) Fe corrodes faster than Al
(4) Group 13 elements have less tendency to form complexes than the *s*-block elements

27. Select the correct statement
(1) Boron is isolated by reducing B_2O_3, with Zn
(2) Boron reacts with acid to form sodium borate and H_2
(3) Lewis acid character is: $BF_3 > BCl_3 > BBr_3 > BI_3$
(4) Disproportionation of ($3Tl^{\oplus} \rightarrow 2Tl + Tl^{+3}$) is less feasible than that of $3Al^{\oplus} \rightarrow 2Al + Al^{+3}$.

28. Select the correct statement
(1) Observed B—Cl distance is shorter than what is expected theoretically in BCl_3 molecule
(2) IE_1 of Al > IE_1 of Ga
(3) Al is obtained by reduction of Al_2O_3 with coke
(4) $AlCl_3$ forms a dimer because Al has high 1E

29. Select the incorrect statement
(1) Ga and In form carbides
(2) Al becomes passive in H_2CrO_4 and $HClO_4$
(3) Cr is extracted from Cr_2O_3 by using Al
(4) W is extracted from WO_3 by using Al

30. Select the incorrect statement
(1) Anodising is electrolysis of H_2SO_4 with Al as anode
(2) In anodising, a film of Al_2O_3 is formed on the surface of Al anode
(3) Thermite mixture used for welding is (Al_2O_3 + Fe) powder
(4) Ga is only superficially oxidised

Compounds of 13 groups

31. On strong heating boric acid yields
(1) B (2) B_2
(3) B_2O_3 (4) B_2H_6

32. Boron trichloride on reaction with water produces 'X' along with HCl. 'X' is
(1) $BOCl_3$ (2) B_2H_6
(3) $B(OH)_3$ (4) B_2O_3

33. Hexaborane(10) is
(1) B_6H_8 (2) B_6H_{10}
(3) B_6H_{12} (4) B_6H_6

34. The name and formula of the compound of boron which is called 'inorganic benzene' are
(1) Borazole, B_6H_6 (2) Borazine, B_6N_6
(3) Borazine, $B_3N_3H_6$ (4) Borazine, $B_6N_3H_3$

35. What is not true about borax?
(1) Molecular formula is $Na_2B_4O_7 \cdot 10H_2O$.
(2) Crystallic borax contains tetranuclear unit of $[B_4O_5(OH)_4]^{2-}$.
(3) It hydrolyses to give an acidic solution.
(4) White crystalline solid.

36. Which hybrid state of boron best explains the structure in B_2H_6 ?
(1) sp^2 (2) sp^3
(3) dsp^2 (4) sp

37. The unexpected order of acidic strength of the trihalides of boron can best be explained by
(1) $p\pi$–$p\pi$ back bonding (2) Hybridisation
(3) Trigonal planar structure (4) None of the above

38. In which of the following, a salt of the type KMO_2 is obtained?
(1) $B_2H_6 + KOH_{(aq)} \longrightarrow$ (2) $Al + KOH_{(aq)} \longrightarrow$
(3) Both (4) None

39. Inorganic graphite is
(1) $B_3N_3H_6$ (2) B_3N_3
(3) SiC (4) P_4S_3

40. Hydrated $AlCl_3$ is used as:
(1) Catalyst in cracking of petroleum
(2) catalyst in Friedel–Crafts reaction
(3) Mordant
(4) All of the above

41. Borax is used as a cleansing agent because on dissolving in water, it gives
(1) Alkaline solution (2) Acidic solution
(3) Bleaching solution (4) Neutral solution

42. Boric acid is polymeric due to:
(1) Its monobasic nature
(2) Its acidic nature
(3) The presence of hydrogen bonds
(4) Its geometry

43. The chemical formula of feldspar is
(1) $KAlSi_3O_8$
(2) Na_3AlF_6
(3) $NaAlO_2$
(4) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$

44. The chief impurity present in bauxite is
(1) SiO_2 (2) Fe_2O_3
(3) K_2SO_4 (4) NaF

45. Al_2O_3 can be converted to anhydrous $AlCl_3$ by heating:
(1) A mixture of Al_2O_3 and carbon in dry Cl_2 gas
(2) Al_2O_3 with HCl gas
(3) Al_2O_3 with Cl_2 gas
(4) Al_2O_3 with NaCl in solid state

46. Boric acid is used in carrom boards for smooth gliding of pawns because
(1) H_3BO_3 molecules are loosely chemically bonded and hence soft.
(2) Its low density makes its fluffy.
(3) It is chemically inert with plywood.
(4) H–bonding in H_3BO_3 gives it a layered structure.

47. Aluminium chloride exits as a dimer, Al_2Cl_6 in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives:
(1) $Al^{3+} + 3Cl^{\ominus}$ (2) $Al_2O_3 + 6HCl$
(3) $[Al(H_2O)_6]^{3+} + 3Cl^{\ominus}$ (4) $[Al(OH)_6]^{3-} + 3HCl$

48. In which of the following molecules is hydrogen bridge bond present?
(1) Water (2) Inorganic benzene
(3) Diborane (4) Methanol

49. Which of the following molecular hydride act as a Lewis acid?
(1) NH_3 (2) H_2O
(3) B_2H_6 (4) CH_4

50. $Na_2B_4O_7 \cdot 10H_2O$ is correctly represented as
(1) $2NaBO_2 \cdot Na_2B_2O_2 \cdot 10H_2O$
(2) $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$
(3) $Na_2[B_4(H_2O)_4O_7] \cdot 6H_2O$
(4) All of the above

51. $AlCl_3$ is an electron-deficient compound but AlF_3 is not, due to
(1) Atomic size of F is smaller than Cl, which makes AlF_3 more covalent.
(2) $AlCl_3$ is a covalent compound while AlF_3 is an ionic compound.
(3) Al in $AlCl_3$ is sp^3 hybridised but in AlF_3, Al is sp^3 hybridised.
(4) $AlCl_3$ exists as a dimer but AlF_3 does not.

52. Bauxite ore is generally contaminated with impurity of oxides of two elements X and Y. Which of the following statement is correct ?
(1) X is a non-metal and belongs to the third period while Y is a metal and belongs to the fourth period.
(2) One of two oxides has three-dimensional polymeric structure.
(3) Both (1) and (2) are correct.
(4) None of the above.

53. The number of isomers possible for disubstituted borazine, $B_3N_3H_4X_2$ is
(1) 3 (2) 4
(3) 6 (4) 5

54. Aqueous solution of borax acts as a buffer because
(1) It contains tribasic acid and strong base.
(2) It contains weak acid and its salt with strong base.
(3) It contains number of neutral water molecules.
(4) None of the above.

55. Correct match is:
(1) Ordinary form of borax : $Na_2B_4O_7 \cdot 5H_2O$
(2) Colemanite : $Ca_2B_6O_{11} \cdot 5H_2O$
(3) Beronarocalcite : $2Mg_3B_8O_{15} \cdot MgCl_2$
(4) Octahedral form of borax : $Na_2B_4O_7 \cdot 10H_2O$

56. Which of the following is acidic in nature?
(1) $Be(OH)_2$ (2) $Mg(OH)_2$
(3) $Al(OH)_3$ (4) $B(OH)_3$

57. Alums are used for:
(1) Tanning of leather (2) Purification of water
(3) Coagulation (4) All of these

58. How can the following reaction be made to proceed in forward direction?
$B(OH)_3 + NaOH \rightleftharpoons Na[B(OH)_4]$
(1) By addition of *cis*-1,2-diol
(2) Addition of borax
(3) Addition of *trans*-1,2-diol
(4) Addition of Na_2HPO_4

59. Borax bead test is responded by:
(1) Divalent metals (2) Heavy metals
(3) Light metals
(4) Metals which form coloured metaborates

60. When excess of NaOH solution is added in potash alum the product is
(1) A bluish precipitate (2) Clear solution
(3) White precipitate (4) Greenish precipitate

61. (3c, 2e) bond is present in
(1) B_2H_6 (2) BCl_3
(3) Al_2Cl_6 (4) NH_3

62. Boron carbide, B_4C, is widely used for:
(1) Making plaster of Paris
(2) Making acetylene
(3) As hardest substance after diamond
(4) Making boric acid

63. BCl_3 does not exist as a dimer but BH_3 exists as B_2H_6 because:
(1) Chlorine is more electronegative than hydrogen.
(2) Large size of chlorine atom does not fit between small-sized boron atoms, while small-sized hydrogen atoms occupy the space between boron atoms.
(3) There is $p\pi$–$p\pi$ back bonding in BCl_3.
(4) Both (2) and (3).

64. Aluminium chloride exits as a dimer because aluminium has:
(1) Greater ionisation enthalpy
(2) Incomplete p-orbital
(3) High nuclear charge
(4) Larger radius

65. Al_2O_3 formation from aluminium and oxygen involves evolution of a large quantity of heat, which makes aluminium use in:
(1) Deoxidiser (2) Confectionary
(3) Thermite welding (4) Indoor photography.

66. A blue coloured mineral 'lapis lazuli' which is used as a semi-precious stone is a mineral of the following class:
(1) Sodium aluminosilicate
(2) Zinc cobaltate
(3) Basic copper
(4) Prussian blue

67. Alum helps in purifying water by:
(1) Forming Si complex with clay particles.
(2) Sulphate part which combines with the dirt and removes it.
(3) Aluminium which coagulates the mud particles.
(4) Making the mud water soluble.

68. Boron halides behave as Lewis acid because of their ______ nature.
(1) Proton donor (2) Covalent
(3) Ionic (4) Electron deficient

69. H_3BO_3 is
(1) Monobasic and weak Lewis acid
(2) Monobasic and weak Bronsted acid
(3) Monobasic and strong Lewis acid
(4) Tribasic and weak Bronsted acid

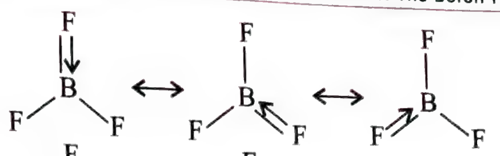
70. Which of the following is not a Lewis acid?
(1) BBr_3 (2) BF_3
(3) BCl_3 (4) $[BH_4]^{\ominus}$

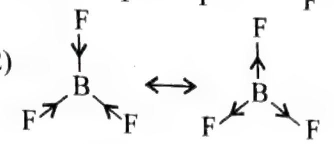
71. The Lewis acid character of halides of boron are as follows:
(1) $BCl_3 > BF_3 > BBr_3$ (2) $BBr_3 > BCl_3 > BF_3$
(3) $BF_3 > BCl_3 > BBr_3$ (4) $BBr_3 > BF_3 > BCl_3$

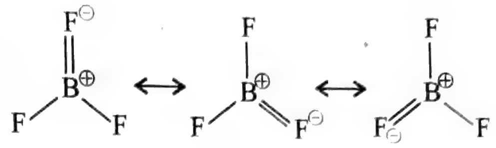
72. Anhydrous $AlCl_3$ is obtained when:
(1) Aluminium oxide reacts with HCl
(2) Aluminium reacts with HCl
(3) Aluminium is heated in a current of dry Cl_2
(4) Aluminium hydroxide reacts with HCl

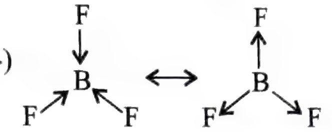
73. Alumina is not used as:
(1) Refractory material
(2) A medium in chromatography
(3) Abrasive
(4) White pigment

74. Which one of the following structures is correctly represented:

(1) 

(2) 

(3) 

(4) 

75. Which one of the following has lowest m.pt.?
(1) B (2) Tl
(3) Al (4) Ga

76. Which one of the following has highest m.pt.?
(1) B (2) Al
(3) Ga (4) Tl

77. In which of the following element +1 oxidation state is more stable:
(1) B (2) Al
(3) Ga (4) Tl

78. Which one is not a borane?
(1) B_5H_9 (2) B_5H_{10}
(3) B_5H_{11} (4) B_6H_{10}

79. The structure of boron nitride resembles that of
(1) Boric acid (2) Graphite
(3) Borazine (4) Borazole

80. When orthoboric acid is heated to red heat the residue is
(1) Boron (2) Boron oxide
(3) Pyroboric acid (4) Metaboric acid

81. Boric acid is a weak monobasic acid and acts as Lewis acid
(1) By donating $H^{\oplus}$
(2) By accepting $\overset{\ominus}{O}H$
(3) By donating lone pair of electrons
(4) By accepting lone pair of electrons.

82. Among group 13 elements the one forming an amphoteric oxide is
(1) Tl (2) Al
(3) B (4) In

83. The stability of monohalides of group 13 elements
(1) Increases down the group.
(2) Decreases down the group.
(3) First increases and then decreases
(4) First decreases and then increases

84. Which is correct for the structure of diborane?
(1) It contains four (2c, 2e) covalent bonds and two (3c, 2e) covalent bonds.

(2) It contains three (2*c*, 2*e*) covalent bonds and three (3*c*, 2*e*) covalent bonds.
(3) It contains two (2*c*, 2*e*) covalent bonds and four (3*c*, 2*e*) covalent bond.
(4) It contains six (2*c*, 2*e*) covalent bonds.

85. Which one is borazole or borazine (inorganic benzene)?
(1) B (2) $B_3N_3H_6$
(3) B_2H_6 (4) B_6H_6

86. Which one of the following is correct statement?
(1) The hydroxides of Al is more acidic than that of B.
(2) The hydroxides of B is basic while that of Al is amphoteric.
(3) The hydroxide of B is acidic, while that of Al is amphoteric.
(4) The hydroxides of B and Al are amphoteric.

87. When Al is added to NaOH solution
(1) No action takes place
(2) $NaAlO_2$ is formed and H_2 is evolved
(3) $Al(OH)_3$ is formed and H_2 is evolved
(4) Na_2AlO_2 is formed and H_2 is evolved

88. Aluminium becomes passive in
(1) Cr_2O_3 (2) Conc HNO_3
(3) $HClO_4$ (4) All of the above

89. Aluminium carbide on hydrolysis produces
(1) Acetylene gas (2) Methane gas
(3) Carbon dioxide gas (4) All of the above

90. The trihalides of group 13 are hydrolysed by water and they fume in moist air due to the
(1) Formation of hydrogen halide
(2) Formation of haloboric acid
(3) Formation of halogen gases
(4) None of the above

91. Diborane is prepared on large scale by
(1) $2BF_{3(g)} + 6LiH_{(s)} \xrightarrow{450\text{ K}} B_2H_{6(g)} + 6LiF_{(s)}$
(2) $2BCl_{3(g)} + 6LiH_{(s)} \xrightarrow{450\text{ K}} B_2H_{6(g)} + 6LiCl_{(s)}$
(3) $2BF_{3(g)} + 6NaH \xrightarrow{450\text{ K}} B_2H_6 + 6NaF$
(4) $2BCl_3 + 6NaH \xrightarrow{450\text{ K}} B_2H_6 + 6NaCl$

92. Which one is covalent compound
(1) $Al_2(SO_4)_3$ (2) Al_2O_3
(3) $AlCl_3$ (4) AlF_3

93. Borax bead test is not given by
(1) Copper salts (2) Cobalt salts
(3) Nickel salts (4) Aluminium salts

94. The borax bead test can be used to detect the presence of
(1) Al (2) Mg
(3) Na (4) Fe

95. Alums can be used for
(1) Purification of water and styptic to arrest bleeding
(2) Mordant in dyeing and in calico printing
(3) In tanning of leather, for sizing of paper and in fire extinguishers
(4) All of the above

96. Which one of the following is not an electron deficient compound
(1) BCl_3 (2) $AlCl_3$
(3) B_2H_6 (4) Al_2Cl_6

97. Borax bead test is based upon the formation of
(1) Metaborates (2) B_2O_3
(3) H_3BO_3 (4) Boron

98. BF_3 is used as a catalyst in several industrial processes due to its:
(1) Strong reducing nature
(2) Weak reducing nature
(3) Strong Lewis acid nature
(4) Weak Lewis acid character

99. Specify the coordination geometry around and the hybridisation of N and B atoms in 1:1 complex of BF_3 and NH_3.
(1) N : tetrahedral, sp^3; B : tetrahedral, sp^3
(2) N : pyramidal, sp^3; B : pyramidal, sp^3
(3) N : pyramidal, sp^3; B : palnar, sp^3
(4) N : pyramidal, sp^3; B : tetrabedral, sp^3

100. Which one of the following is the correct statement?
(1) $B_2H_6{\cdot}2NH_3$ is known as inorganic benzene.
(2) Boric acid is a protonic acid.
(3) Beryllium exhibits a coordination number of six.
(4) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase.

101. In the structure of $[B_4O_5(OH)_4]^{2-}$
(1) All four B atoms are trigonal planar.
(2) One B atom is tetrahedral and the other three B atoms are trigonal planar.
(3) Three B atoms are tetrahedral and one B atom is trigonal planar
(4) Two B atoms are tetrahedral and other two are trigonal planar

102. The pH of an aqueous solution of Al^{3+} is likely to be
(1) Neutral (2) Acidic
(3) Slightly basic (4) Highly basic

103. In the reaction:
$2X + B_2H_6 \longrightarrow [BH_2(X_2)]^{\oplus}[BH_4]^{\ominus}$
Which of the following is not 'X'?
(1) NH_3 (2) CH_3NH_2
(3) $(CH_3)_2NH$ (4) $(CH_3)_3N$

104. $B_{10}C_2H_{12}$ is isoelectronic with
(1) $(B_{12}H_{12})^{2-}$ (2) $B_{12}H_{12}$
(3) $(B_{12}H_{12})^{2+}$ (4) $(B_{12}H_{12})^{\oplus}$

105. The correct order of the atoms in terms of their IE_1 is:
(1) Li < B < Be < C (2) Li < Be < B < C
(3) Li > B > Be > C (4) Li > Be > B > C

106. B_2H_6 is:
(1) $(2C-3e^-)$ compound
(2) an odd e^--deficient compound
(3) an electron deficient compound
(4) a sp^2 hybridized compound

107. $NaBH_4$ is:
(1) Reducing agent (2) Oxidising agent
(3) Bleaching agent (4) Complexing agent.

108. Select incorrect statements
(1) Borax in its crystal possess 2 tetrahedral and 2 plane triangular units
(2) Aluminium vessels are not washed with washing soda
(3) Stability of $Tl^{\oplus} > In^{\oplus} > Ga^{\oplus}$
(4) BCl_3 is not hydrolyzed while $SiCl_4$ can be hydrolyzed.

109. Select the incorrect statement about B_2H_6.
(1) B is sp^3 hybridized
(2) There are two terminal B—H bonds for each B-atom
(3) There are only 12 bonding electrons available
(4) B—H—B angle is 180°.

110. $Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} (A) + NaBO_2 + H_2O$
$(A) + Cr_2O_3 \xrightarrow{\Delta} (B)$
Compound (A) and colour of compound (B) is:
(1) B_2O_3, Blue (2) Na_3BO_3, Blue
(3) B_2O_3, Green (4) Na_3BO_3, Green

111. Select the incorrect statement about borax.
(1) It is a useful primary standard for titrating against acids.
(2) Its aqueous solution can be used as buffer
(3) In its structure out of 10 molecules of H_2O, four H_2O molecules are part of its structure
(4) sp^2 hybridised B-atoms only participate in $(p\pi - p\pi)$ back bonding

112. The given reaction can proceed in forward direction by the addition of:
$B(OH)_3 + NaOH \longrightarrow Na[B(OH)_4] + NaBO_2 + H_2O$
(1) Borax (2) Na_2HPO_4
(3) *Trans*-1, 2-diol (4) *Cis*-1, 2-diol

113. $4LiBH_4 + SiCl_4 \longrightarrow SiH_4 + 4LiCl + (X)$
The *incorrect* statement about (X) in the above reaction is
(1) $4(2e^- - 2C)$ bonds
(2) $12e^-$'s are involved in bonding
(3) $2(2e^- - 3C)$ bonds
(4) 'X' does not react with NH_3

Multiple Correct Answers Type

Physical and chemical properties

1. Stability of monovalent and trivalent cations of Ga, In, Tl lie in following sequence:
(1) $Ga^{3+} < In^{3+} > Tl^{3+}$ (2) $Ga^{3+} > In^{3+} > Tl^{3+}$
(3) $Tl^{\oplus} > In^{\oplus} > Ga^{\oplus}$ (4) $Ga^{\oplus} < In^{\oplus} > Tl^{\oplus}$

2. Which of the following metals are extracted by using Al as reducing agent ?
(1) Na from Na_2O (2) Cr from Cr_2O_3
(3) W from WO_3 (4) Mg from MgO

3. Aluminium becomes passive in:
(1) conc. HNO_3 (2) H_2CrO_4
(3) $HClO_4$ (4) conc. HCl

4. Possible oxidation states of boron family elements are:
(1) +1 (2) +2
(3) +3 (4) +4

5. Which of the following element do not form carbide?
(1) B (2) Al
(3) In (4) Ga

6. Gallium has smaller atomic radius than aluminium because of
(1) Poor shielding power of *d* electrons of Ga atom
(2) Poor shielding power of *s* electrons of Ga atom
(3) Greater shielding power of *s* electrons of Al atom
(4) Greater shielding power of *d* electrons of Ga atom

7. Which of the following compound(s) undergo disproportionation in aqueous solution?
(1) $TlCl_3$ (2) GaCl
(3) InCl (4) TlCl

8. Which of the following statements are correct for Al?
(1) Bad conductor of electricity
(2) Malleable and ductile
(3) Found free in nature
(4) Alloys of Al are light

9. Alumina is
(1) A bad conductor of electricity
(2) Good conductor of electricity
(3) A dehydrating agent
(4) Insoluble in water

10. Which of the following minerals contain aluminium ?
(1) Fluorspar (2) Feldspar
(3) Mica (4) Carborundum

11. BCl_3 has
(1) a planar trigonal structure
(2) an electron deficient compound
(3) zero dipole moment
(4) a Lewis base

12. Select incorrect statements
(1) Anhydrous aluminium chloride (Al_2Cl_6), a covalent compound and soluble in water giving, $[Al(H_2O)_6]^{3+}$ and $Cl^{\ominus}$ ions
(2) $BX + NH_3 \xrightarrow[\text{Temperature}]{\text{Room}} \underset{\text{Adduct}}{(H_3N: \rightarrow BX_3)}$
The heat of adduct formation is maximum for BF_3
(3) Alumina (Al_2O_3) is insoluble in H_2O due to high heat of hydration and low lattice energy.
(4) $B_3N_3H_6$ is an electron deficient compound

13. Select correct statements
(1) Colour of the bead in borax bead test is mainly due to the formation of metal meta-borates
(2) Borax on reaction with mineral acid gives orthoboric acid.
(3) $(AlCl_3)_n$ sublimes on heating
(4) $B_2H_6(g)$ is obtained by the reaction of NaH or $NaBH_4$ with BF_3 under anhydrous condition

14. Select correct statements
(1) Borate salts when heated with conc. H_2SO_4 and C_2H_5OH produces characteristics green colouration on flame due to the formation of volatile $(C_2H_5)_3B$
(2) In potash alum, each Al^{+3} ion is surrounded by 24 molecules of H_2O
(3) BH_3 exists as dimer
(4) BCl_3 does not exist as dimer

15. Select incorrect statements
(1) EN of Al = 2.0, En of O = 3.5. From EN values alumina is ionic compound
(2) Diborane at low temperature on reaction with NH_3 for borazole.
(3) Diborane at high temperature on reaction with NH_3 forms an adduct
(4) Boron carbide is B_4C or $B_{12}C_3$

16. Select correct statements
(1) Borazole shows addition reaction and with Cl_2 produces $B_3N_3H_9Cl_3$ in which Cl is bonded to N-atom
(2) In Al_2Cl_6, the angle Cl–Al–Cl is 110° and 93° and the angle Al–Cl–Al is 87°
(3) Four Al–Cl bonds are of same length and two of different length
(4) $Al_2(SO_4)_3$ on reaction with NH_4OH produce SO_3 gas

Compounds of 13 groups

17. Which of the following oxides are basic?
(1) B_2O_3 (2) Tl_2O
(3) In_2O_3 (4) Al_2O_3

18. $Al_2(SO_4)_3 + NH_4OH \longrightarrow X$; X is
(1) A white gelatinous precipitate
(2) Soluble in excess of NH_4OH
(3) Soluble in excess of NaOH
(4) Amphoteric in nature

19. Which of the following statements are true for H_3BO_3?
(1) It is weak monobasic acid and a Lewis acid.
(2) It does not act as a proton donor but acts as an acid by accepting hydroxyl ions.
(3) It has a layer structure in which BO_3 units are joined by van der Waals forces of attraction.
(4) It is obtained by treating borax with conc H_2SO_4.

20. In the reaction
$$2X + B_2H_6 \longrightarrow [BH_2X_2]^{\oplus} [BH_4]^{\ominus}$$
the amine(s) X is (are):
(1) NH_3 (2) CH_3NH_2
(3) $(CH_3)_2NH$ (4) $(CH_3)_3N$

21. Select the correct statements about diborane:
(1) B_2H_6 has three-centre two electron bond
(2) Each boron atom lies in sp^3 hyrid state
(3) $H_b \ldots B \ldots H_b$ bond angle is 122°
(4) All hydrogens in B_2H_6 lie in the same plane

22. Orthoboric acid (H_3BO_3) and metaboric acid (HBO_2) differ in respect of:
(1) Basicity (2) Structure
(3) Melting point (4) Oxidation

23. Diborane reacts with ammonia under different conditions to give:
(1) $B_2H_6 \cdot 2NH_3$ (2) $B_{12}H_{12}$
(3) $B_2N_3H_6$ (4) $(BN)_x$

24. BF_3 is
(1) Electron-deficient compound
(2) Lewis acid
(3) Used as rocket fuel
(4) Ionic compound

25. Boric acid is prepared from borax by the action of
(1) HCl (2) NaOH
(3) CO_2 (4) H_2SO_4

26. Which of the following are incorrect statements?
(1) BH_3 is a stable compound.
(2) Boron hydrides are readily hydrolysed.
(3) Boron hydrides are formed by the reation of Mg_3B_2 and dil HCl.
(4) All B–H bonds in B_2H_6 are equal.

27. Potash alum is used as a
(1) Disinfectant
(2) Water softener
(3) Mordant in textile industry
(4) Fibre in polymer industry

28. Boranes have general formula:
(1) B_nH_{n+2} (2) B_nH_{2n+2}
(3) B_nH_{n+4} (4) B_nH_{n+6}

29. Double sulphates of a divalent and trivalent metal crystallised with 24 molecules of water of crystallisation are called pseudoalums and are not isomorphous with true alums. Which of them is/are pseudoalums?
(1) $MnSO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
(2) $FeSO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
(3) $ZnSO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
(4) $CaSO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

Linked Comprehension Type

Paragraph 1

The heavier members of 13 and 14 groups besides the group oxidation state also show another oxidation state which is two units less than the group oxidation state. Down the group (↓), the stability of higher oxidation state decreases and that of lower

xidation state increases. This concept which is commonly called ert pair effect has been used to explain many physical and mical properties of the element of these groups.

1. Heavier members of group 13 exhibit oxidation state
(1) +3 only (2) +1 only
(3) +1 and +3 both (4) +1, +2, +3

2. Which among the following is the strongest oxidising agent?
(1) SiO_2 (2) GeO_2
(3) SnO_2 (4) PbO_2

3. Which among the following is the strongest reducing agent?
(1) GaCl (2) InCl
(3) BCl_3 (4) TlCl

4. The strongest reductant among the following is
(1) $SnCl_2$ (2) $SnCl_4$
(3) $PbCl_2$ (4) $GeCl_2$

5. Which of the following statement is wrong ?
(1) Tl(III) salt undergo disproportionation.
(2) CO is used as a reducing agent.
(3) CO_2 is a greenhouse gas.
(4) SiO_2 is a covalent solid.

6. Which of the following act as the strongest acid?
(1) Tl_2O_3 (2) SnO_2
(3) PbO_2 (4) CO_2

aragraph 2

espite the fact that aluminium is a reactive metal, it is stable in r as well as in water. This is due to the formation of thin layer of ide on the surface of aluminium metal which makes it passive r further attack. The layer is so useful, that in industry, it is rposely deposited by an electrolytic process called anodising. action of aluminium with oxygen is highly exothermic and is lled thermite reaction.

$$Al_{(s)} + \frac{3}{2} O_{2(g)} \longrightarrow Al_2O_{3(s)} \qquad \Delta_f H^{\ominus} = -1670 \text{ kJ mol}^{-1}$$

is reaction finds application for welding of metals and in the etallurgical extraction of many metals from their oxides. The mitation is that to start the reaction, high temperature is required r which an ignition mixture is required.

7. Which of the following metals cannot be extracted by using Al as a reducing agent?
(1) W from WO_3 (2) Mn from Mn_3O_4
(3) Cr from Cr_2O_3 (4) Na from Na_2O

8. Aluminium becomes passive in:
(1) H_2CrO_4 (2) conc HNO_3
(3) $HClO_4$ (4) NaOH

9. Anodising can be done by electrolysing dil H_2SO_4 with Al as anode. This results in:
(1) Formation of $Al_2(SO_4)_3$ on the surface of Al anode
(2) Formation of Al_2O_3 on the surface of Al anode
(3) Formation of polymeric aluminium hydride film on the surface of Al anode
(4) None of the above

10. The reaction which is not involved in thermite process is
(1) $2Fe + Al_2O_3 \longrightarrow Fe_2O_3 + 2Al$
(2) $B_2O_3 + 2Al \longrightarrow 2B + Al_2O_3$
(3) $3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3$
(4) $Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$

11. Thermite mixture used for welding is
(1) Fe_2O_3 and Al powder (2) BaO and Mg powder
(3) Fe and Al (4) Cu and Al

12. Anodised aluminium is
(1) Al obtained at anode
(2) Al prepared electrolytically
(3) Alloy of Al containing 95% Al
(4) Al electrolytically coated with Al_2O_3

Paragraph 3

$$\text{Colemanite} + Na_2CO_3 \xrightarrow{\text{Fused}} (A) + (B) + CO_2$$

$$\underset{\text{Solution}}{(A)} + CO_2 \longrightarrow (B) + Na_2CO_3$$

$$(B) + \text{conc HCl} \longrightarrow NaCl + \underset{\text{Acid}}{(C)}$$

$$\underset{\text{Acid}}{(C)} + H_2O \longrightarrow \underset{\text{Acid}}{(D)}$$

$$(D) \xrightarrow{\text{Strong heating}} (E)$$

$$(E) + CuSO_4 \xrightarrow[\text{inflame}]{\text{Heated}} \underset{\text{Blue-coloured compound}}{(F)}$$

13. Colemanite is
(1) $Ca_2B_2O_{11}$ (2) $Ca_2B_6O_{11}$
(3) $Ca_4B_4O_{11}$ (4) $Ca_6B_6O_{11}$

14. Compound (A) is
(1) $NaBO_2$ (2) $Na_2B_4O_7$
(3) Na_3BO_3 (4) NaOH

15. Compound (B) is
(1) $Na_2B_4O_7$ (2) $NaBO_2$
(3) Na_3BO_3 (4) NaOH

16. Compound (C) is
(1) $H_2B_4O_7$ (2) HBO_2
(3) H_3BO_3 (4) H_2O

17. Compound (D) is
(1) $H_2B_4O_7$ (2) HBO_2
(3) H_3BO_3 (4) H_2O

18. Compound (E) is
(1) B_2O_3 (2) B
(3) H_3BO_3 (4) None of these

19. Compound (F) is
(1) CuS (2) Cu_2O
(3) $CuSO_3$ (4) $Cu(BO_2)_3$

Paragraph 4

Boron with hydrogen forms a number of hydrides which are known as boranes. These hydrides are classified into closoboranes and nidobaranes. The simplest hydride of boron is diborane. Boron apart from having (2*c*, 2*e*) bonds also contain (3*c*, 2*e*) bonds.

20. General formula of closoboranes is
(1) B_nH_{n+4} (2) B_nH_{n+6}
(3) B_nH_{n+2} (4) B_nH_{n-4}

21. General formula of nidoboranes is
(1) B_nH_{n+4} (2) B_nH_{n+6}
(3) B_nH_{n+2} (4) B_nH_{n-4}

22. Diborane is
(1) B_2H_6 (2) B_2H_8
(3) B_2H_2 (4) B_2H_7

23. Boron in diborane is _____ hydridised.
(1) *sp* (2) sp^2
(3) sp^3 (4) dsp^2

24. Three centre two electron (3*c*, 2*e*) bond is present in:
(1) BCl_3 (2) $B(OH)_3$
(3) B_2H_6 (4) B_4H_{10}

25. In B_2H_6,
(1) There is B–B bond
(2) All the atoms are in one plane
(3) The boron atoms are linked through hydrogen bridges
(4) All the B–H bond distances are equal

26. Which of following is an electron-deficient compound?
(1) B_2H_6 (2) B_4H_{10}
(3) CH_4 (4) NH_3

Paragraph 5

Boron reacts with oxygen at 700°C to give (A). Compound (A) reacts with carbon and dry chloride to give (B) and carbon monoxide. (B) on reduction with $LiAlH_4$ gives (C) along with LiCl and $AlCl_3$. (C) on reaction with ammonia gives (D), which on heating gives (E). (C) on reaction with NaH gives (F).

27. Compound (A) is
(1) BO_3 (2) B_2O_3
(3) BO_2 (4) B_4O_6

28. In compound (B):
(1) Boron is sp^2 hybridised
(2) B is triangular planar molecule
(3) It is a Lewis base
(4) Dimer

29. Compound (C) is
(1) An electron-deficient compound
(2) Contain (3*c*, 2*e*) bond
(3) Has ethane like structure
(4) An ionic compound.

30. Compound (D) has B in ________ hybridised state
(1) *sp* (2) sp^2
(3) sp^3 (4) dsp^2

31. Compound (E) is
(1) Inorganic benzene (2) Borazine
(3) Borazon (4) Diborane

32. Compound (F) behaves as
(1) Reducing agent (2) Oxidising agent
(3) Complexon (4) Buffer

33. Compound (B) and (C) are ______ and ______ respectively
(1) BCl_3, B_2H_6 (2) BCl_3, B_4H_{10}
(3) B_2Cl_6, B_2H_6 (4) BCl_3, B_4H_{10}

Paragraph 6

Borax is actually made of two tetrahedra and two triangular units joined together and should be written as

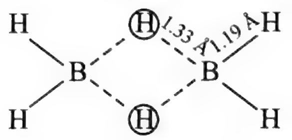
$Na_2[B_4O_5(OH)_4]\cdot 8H_2O$

34. Consider the following statements about borax:
A : Each boron atom has four B—O bonds.
B : Each boron atom has three B—O bonds.
C : Two boron atoms have four B—O bonds while other two have three B—O bonds.
D : Each boron atom has one—OH group.
Select correct statement(s):
(1) A, B (2) B, C
(3) C, D (4) A,C

35. Select the correct statement(s):
(1) Borax is used as a buffer.
(2) 1 M borax solution reacts with equal volumes of 2 M HCI solution.
(3) Titration of borax can be done by using methyl orange as the indicator.
(4) Coloured bead obtained in borax-bead test contains metaborate.

Paragraph 7

The molecular shapes of diborane is shown below:



36. Consider the following statements for diborane:
i. Boron is approximately sp^3 hybridised
ii. B—H—B angle is 180°
iii. There are two terminal B—H bonds for each boron atom.
iv. There are only 12 bonding electrons available
Of these statements:
(1) i, iii and iv are correct (2) i, ii and iii are correct
(3) ii, iii and iv are correct (4) i, ii and iv are correct

37. Select correct statement about B_2H_6:
(1) Bridging groups are electron-deficient with 12 valence electrons.
(2) It has (2*c*, 2*e*) B—H bonds.
(3) It has (3*c*, 2*e*) B—H—B bonds.
(4) All of the above are correct statements.

Matrix Match Type

This section contains questions each with two colums I and II. Match the items in column I with that in the column II.

1.

	Column I		Column II
a.	Corundum	i.	$Ca_2B_6O_{11}\cdot 5H_2O$
b.	Cryolite	ii.	$Al_2O_3\cdot 2H_2O$
c.	Potash alum	iii.	Sodium aluminium fluoride
d.	Colemanite	iv.	Al_2O_3
e.	Bauxite	v.	$Na_2B_4O_7\cdot 10H_2O$
f.	Borax	vi.	$K_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O$

2.

	Column I		Column II
a.	Alum	i.	Antiseptic
b.	Borax	ii.	Alloy
c.	Ultramarine	iii.	Friedel–Crafts reaction
d.	Anhydrous $AlCl_3$	iv.	Complex blue-coloured silicate
e.	Magnelium	v.	Tincal
f.	Diborane	vi.	(3*c*, 2*e*) bond

3.

	Column I		Column II
a.	Inorganic benzene	i.	Diamond
b.	Inorganic graphite	ii.	Mordant
c.	Jeweller's borax	iii.	BN
d.	Alum	iv.	$B_3N_3H_6$
e.	Lubricating agent	v.	$Na_2B_4O_7\cdot 5H_2O$
f.	An abrasive	vi.	Graphite

4.

	Column I		Column II
a.	Good thermal conductivity	i.	Utensils
b.	Non-toxicity	ii.	Building ships and aircrafts
c.	Good electrical conductivity	iii.	Adsorbent
d.	Low density and resistance to corrosion	iv.	Food packing
e.	Gel nature of $Al(OH)_3$	v.	Electric wires
f.	Lead pencil	vi.	Graphite

5.

	Column I		Column II
a.	Boric acid	i.	$Na_2[B_4O_5(OH)_4]$
b.	Kernite	ii.	$K_2O\cdot 3Al_2O_3\cdot 6SiO_2\cdot 2H_2O$
c.	Feldspar	iii.	$Al_2O_3\cdot 2SiO_2\cdot 2H_2O$
d.	Mica	iv.	$KAlSi_3O_8$
e.	Kaolinite	v.	H_3BO_3
f.	Diaspore	vi.	$Al_2O_3\cdot H_2O$

6.

	Column I		Column II
a.	$B_2H_6 + \underset{\text{(excess)}}{NH_3} \xrightarrow{\Delta}$	i.	H_3BO_3
b.	$B_2H_6 + H_2O \longrightarrow$	ii.	BN
c.	$BCl_3 + LiAlH_4 \longrightarrow$	iii.	$NaNO_2 + B_2O_3$
d.	Borax $\xrightarrow{\Delta}$	iv.	B_2H_6

7. Match the items given in Column I with that in the Column II and III.

	Column I Compound		Column II Characteristics (I)		Column III Characteristics (II)
a.	Borax	i.	$M_2^{+1}SO_4.\ M_2^{+3}(SO_4)_3.24H_2O$.	p.	sp^3, (3c, 2$\bar{e}$) bond
b.	Borazole	ii.	B_2H_6	q.	Both sp^2 and sp^3 hydridised B atoms
c.	Nidoboarane	iii.	$M^{+2}SO_4\ M^{+3}{}_2(SO_4)_3.24H_2O$	r.	Ring structure with alternate BH and NH groups
d.	Alums	iv.	On heating it gives a transparent glass like bead	s.	Each metal is surrounded by six water molecules
e.	Pseudo alums	v.	$3B_2H_6+6NH_3 \downarrow 3[BH_2(NH_3)_2]^{\oplus}[BH_4]^{\ominus} \downarrow\Delta\ 2B_3N_3H_6 + 12H_2$	t.	More reactive than benzene

For Q.8 to Q.11

Answer the questions given below by appropriately matching the information given in three column of the following table.

S. No.	Column I E.C. of 13 group elements		Column II Characteristics (I)		Column III Characteristics (II)
a.	$6s^2, 6p^1$	i.	Lowest atomic radii	p.	Basic oxides
b.	$3s^2, 3p^1$	ii.	Its (+1) compounds are toxic as they upset the enzyme systems in the body	q.	Icosahedron structure
c.	$4s^2, 4p^1$	iii.	highest boiling point in the group	r.	Amphoteric oxides
d.	$2s^2, 2p^1$	iv.	Its trihalides exists as a dimer	s.	Acidic oxides
				t.	Lowest melting point and exists as liquid at room temperature

8. For aluminium, correct combination is:
   (1) b–iv–r (2) c–i–r, t
   (3) c–i–r (4) c–i–t
9. For gallium, correct combination is:
   (1) c–i–r (2) c–i–t
   (3) c–i–r, t (4) b–iv–r
10. For thallium, correct combination is:
    (1) c–i–r, t (2) c–i–r
    (3) c–i–t (4) a–ii–p
11. For boron, correct combination is:
    (1) d–iii–q (2) d–iii–q, s
    (3) d–iii–s (4) b–iv–r

Numerical Value Type

1. What is the value of 'x' in the silicate mineral, $Be_3Al_2Si_xO_{18}$?
2. What is the value of 'x' in colemanite, $Ca_2B_xO_{11} \cdot 6H_2O$?
3. How much nitrogen is evolved when one gram of ammonium chloride is heated with borax strongly?
4. How many orbitals of boron are involved in the hybridisation in B_2H_6?
5. Borax is correctly represented as $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$. How many tetrahedral boron atoms are present in the structure of borax?
6. How many isomers of $B_3N_3H_4X_2$ are possible?
7. How many water molecules of crystallisation are present in crystalline aluminium chloride?
8. How many water molecules of crystallisation are present in borax, $Na_2B_4O_7 \cdot 10H_2O$?
9. How many moles of NO_2 are produced when mole of B reacts with HNO_3?

Archives

JEE MAIN

Single Correct Answer Type

1. Boron can't form which one of the following anions?
   (1) BF_6^{3-} (2) BH_4^-
   (3) $B(OH)_4^-$ (4) BO_2^- **(AIEEE 2011)**

JEE ADVANCED

Single Correct Answer Type

1. In the context of the Hall–Heroult process for the extraction of Al, which of the following statements is false?
   (1) CO and CO_2 are produced in this process
   (2) Al_2O_3 is mixed with CaF_2 which lowers the melting point of the mixture and brings conductivity
   (3) Al^{3+} is reduced at the cathode to form Al
   (4) Na_3AlF_6 serves as the electrolyte

   (JEE Advanced 2015)
2. The increasing order of atomic radii of the following Group 13 elements is
   (1) Al < Ga < In < Tl (2) Ga < Al < In < Tl
   (3) Al < In < Ga < Tl (4) Al < Ga < Tl < In

   (JEE Advanced 2016)

Multiple Correct Answers Type

1. In the following reaction,

   $2X + B_2H_6 \longrightarrow [BH_2(X)_2]^{\oplus} [BH_4]^{\ominus}$

   The amine(s) X is/are
   (1) NH_3 (2) CH_3NH_2
   (3) $(CH_3)_2NH$ (4) $(CH_3)_3N$

   (IIT-JEE 2009)
2. The correct statement(s) for orthoboric acid is/are
   (1) It behaves as a weak acid in water due to self-ionization
   (2) Acidity of its aqueous solution increases upon addition of ethylene glycol
   (3) It has a three-dimensional structure due to hydrogen bonding
   (4) It is a weak electrolyte in water

   (JEE Advanced 2014)

3. The crystalline form of borax has
(1) tetranuclear $[B_4O_5(OH)_4]^{2-}$ unit
(2) all boron atoms in the same plane
(3) equal number of sp^2 and sp^3 hybridized boron atoms
(4) one terminal hydroxide per boron atom

(JEE Advanced 2016)

4. Among the following, the correct statement(s) is(are)
(1) $Al(CH_3)_3$ has the three-centre two-electron bonds in its dimeric structure
(2) BH_3 has the three-centre two-electron bonds in its dimeric structure
(3) $AlCl_3$ has the three-centre two-electron bonds in its dimeric structure
(4) The Lewis acidity of BCl_3 is greater than that of $AlCl_3$

(JEE Advanced 2017)

Numerical Value Type

1. The coordination number of Al in the crystalline state of $AlCl_3$ is ________. **(IIT-JEE 2009)**
2. Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is **(JEE Advanced 2015)**

Answers Key

EXERCISES

Single Correct Answer Type

1. (1) 2. (3) 3. (1) 4. (4) 5. (4)
6. (1) 7. (1) 8. (2) 9. (2) 10. (3)
11. (1) 12. (3) 13. (4) 14. (1) 15. (1)
16. (2) 17. (3) 18. (4) 19. (3) 20. (1)
21. (1) 22. (1) 23. (3) 24. (1) 25. (3)
26. (4) 27. (4) 28. (1) 29. (1) 30. (3)
31. (3) 32. (3) 33. (2) 34. (3) 35. (3)
36. (2) 37. (1) 38. (3) 39. (2) 40. (3)
41. (3) 42. (3) 43. (1) 44. (2) 45. (1)
46. (1) 47. (3) 48. (3) 49. (3) 50. (2)
51. (2) 52. (3) 53. (2) 54. (2) 55. (2)
56. (4) 57. (4) 58. (1) 59. (4) 60. (2)
61. (1) 62. (3) 63. (3) 64. (2) 65. (3)
66. (1) 67. (3) 68. (4) 69. (1) 70. (4)
71. (2) 72. (3) 73. (3) 74. (1) 75. (4)
76. (1) 77. (4) 78. (2) 79. (2) 80. (2)
81. (2) 82. (2) 83. (1) 84. (1) 85. (2)
86. (3) 87. (2) 88. (2) 89. (2) 90. (1)
91. (1) 92. (3) 93. (4) 94. (4) 95. (4)
96. (4) 97. (1) 98. (3) 99. (1) 100. (4)
101. (4) 102. (3) 103. (4) 104. (1) 105. (1)
106. (3) 107. (1) 108. (4) 109. (4) 110. (3)
111. (3) 112. (4) 113. (4)

Multiple Correct Answers Type

1. (2, 3) 2. (2, 3) 3. (1, 2, 3)
4. (1, 3) 5. (3, 4) 6. (1, 2, 3)
7. (2, 3) 8. (2, 4) 9. (1, 4)
10. (2, 3) 11. (1, 2, 3) 12. (1, 2, 3, 4)
13. (1, 2, 3, 4) 14. (3, 4) 15. (1, 2, 3)
16. (2, 4) 17. (2, 3) 18. (1, 3, 4)
19. (1, 2, 4) 20. (1, 2, 3) 21. (1, 2, 3)
22. (1, 2, 3) 23. (1, 3, 4) 24. (1, 2)
25. (1, 4) 26. (1, 4) 27. (1, 2)
28. (3, 4) 29. (1, 2)

Linked Comprehension Type

1. (3) 2. (4) 3. (1) 4. (4) 5. (1)
6. (4) 7. (4) 8. (1,2,3) 9. (1) 10. (1)
11. (1) 12. (4) 13. (2) 14. (1) 15. (1)
16. (1) 17. (3) 18. (1) 19. (4) 20. (1)
21. (2) 22. (1) 23. (3) 24. (3,4) 25. (3)
26. (1,2) 27. (2) 28. (1,2) 29. (1,2) 30. (2)
31. (1,2) 32. (1) 33. (1) 34. (3) 35. (1,2,3,4)
36. (1) 37. (4)

Matrix Match Type

Q. No.	a	b	c	d	e	f
1.	iv	iii	vi	i	ii	v
2.	i	v	iv	iii	ii	vi
3.	iv	iii	v	ii	vi	i
4.	i	iv	v	ii	iii	vi
5.	v	i	iv	ii	iii	vi

6. (a → q, b → p, c → s, d → r,)
7. (a → iv-q; b → v-r, t; c → ii-p; d → i-s; e → iii-s)
8. (1) 9. (3) 10. (4) 11. (2)

Numerical Value Type

1. (6) 2. (6) 3. (0) 4. (4) 5. (2)
6. (4) 7. (6) 8. (8) 9. (3)

ARCHIVES

JEE Main

Single Correct Answer Type

1. (1)

JEE Advanced

Single Correct Answer Type

1. (4) 2. (2)

Multiple Correct Answers Type

1. (1, 2, 3) 2. (2, 4) 3. (1, 3, 4)
4. (1, 2, 4)

Numerical Value Type

1. (6) 2. (6)

7 p-Block Group 14 Elements The Carbon Family

OVERVIEW

Group 14 Elements: The Carbon Family

1. Group 14 of the periodic table constitutes carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb).
2. **Occurrence:**
   a. Carbon is the seventeenth and silicon is the second most abundant element by mass in the earth's crust.
   b. Carbon is found in both native and combined states.
   c. Silicon is present in nature as silica, SiO_2 (sand and quartz).
   d. Germanium occurs in traces.
   e. Tin occurs as cassiterite or tinstone, SnO_2.
   f. The principal ore of lead is galena, PbS.
3. **Atomic and physical properties:**
   a. General electronic configuration: $ns^2\ np^2$.
   b. Electronic configuration of C and Si differs from that of Ge, Sn and Pb. C and Si have noble gas core beneath the valence shell, whereas Ge, Sn and Pb have fully filled lesser shielding *d* and/or *f*-orbital in-between the valence shell and the noble gas core.
   c. Covalent radii: C > Si > Ge > Sn > Pb.
   d. Ionisation enthalpy: C > Si > Ge > Pb > Sn.
   e. Electronegativity: C > Si; after Si, electronegativity remains constant from Si to Sn.
   f. Non-metallic character decreases, or metallic character increases, down the group (↓)

   $$\underbrace{\text{C}\quad \text{Si}}_{\text{Non-metals}}\qquad \underbrace{\text{Ge}}_{\text{Metalloid}}\qquad \underbrace{\text{Sn}\quad \text{Pb}}_{\text{Metals}}$$

   g. Melting point and boiling point decrease down the group.
4. All the elements show tetravalency as the promotional energy required to unpair and promote an electron from *ns* to *np* is more than the energy compensated by the bond energy released during MX_4 formation.
5. **Oxidation states:**
   a. Due to inert pair effect, C and Si exhibit +4 oxidation state, whereas Ge, Sn and Pb show +4 and +2 oxidation states.
   b. Stability of +4 oxidation decreases in the order: Ge > Sn > Pb. Tendency to behave as oxidising agent increases down the group, i.e. Ge < Sn < Pb, i.e. Pb(IV) compounds are strongest oxidising agents.
   c. Stability of lower oxidation state (+2) increases in the order: Ge < Sn < Pb. Tendency to behave as reducing agents decreases down the group: Ge > Sn > Pb, i.e. Ge(II) compounds are the strongest reducing agent.
   d. Pb(II) compounds are more stable than Pb(IV) compounds; thus, Pb(IV) compounds act as strong oxidising agent.
6. Carbon shows the maximum covalency of 4, whereas Si, Ge, Sn and Pb show the maximum covalency of 6. This is due to the absence of vacant *d*-orbitals in C and the presence of these orbitals in the valence shell in Si, Ge, Sn and Pb.
7. On heating with oxygen O_2, group 14 elements form oxides of the type MO_2.

   $$\underbrace{CO_2\quad SiO_2}_{\text{Acidic}}\qquad \underbrace{GeO_2}_{\text{Amphoteric}}\qquad \underbrace{SnO_2\quad PbO_2}_{\text{weakly basic}}$$
   $$\xrightarrow[\text{Acidic nature decreases}]{}$$

   They dissolve in alkali (e.g. NaOH) to form carbonates, silicates, germanates, stannates and plumbates of the type Na_2MO_3.
8. **Hydrides:** All group 14 elements form covalent hydrides. Down the group (↓), the number of stable hydrides and ease with which these are formed decreases due to decrease in M–M and M–H bond strength. Hydrides are gaseous. Down the group, their thermal stability decreases, and consequently their reducing nature increases.

   Thermal stability: $CH_4 < SiH_4 < GeH_4 < SnH_4 < PbH_4$
   Reducing nature: $CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$
9. All group 14 elements form tetrahalides of the type MX_4, except lead which forms $PbBr_4$ and PbI_4. These halides are covalent and formed by sp^3 hydridisation. The thermal stability decreases in the order:

   $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$

   Except carbon halides, all other halides are readily hydrolysed by water due to the presence of vacant *d*-orbitals. Tetrahalides behave as strong lewis acids and readily form complexes.

10. The ability of the atoms of the same element to link with one another by a covalent bond to form long chains, branched or cyclic compounds, is known as *catenation*. Carbon exhibits the unique tendency for catenation. The catenating ability decreases down the group:

C >> Si > Ge > Sn > Pb

Lead shows no catenating ability.

11. The phenomenon by which an element exists in two or more crystalline and amorphous forms, differing in physical properties but having almost similar chemical properties, is known as **allotropy**. The phenomenon of allotropy arises due to differences in:

a. The arrangement of atoms in the lattice structure.

b. The number of atoms in the molecule.

c. The method of crystallisation.

Allotropes of carbon:

a. Crystalline	• Diamond • Graphite *(thermodynamically most stable)* • Fullerenes
b. Amorphous or microcrystalline forms	• Coke • Charcoal • Lamp black
Allotropes of silicon	• Amorphous • Crystalline
Allotropes of tin	• Grey • White (most stable) • Rhombic

12. Diamond:
- Purest form of carbon
- Crystalline
- Hardest natural substance known
- Bad conductor of heat and electricity
- Transparent to X rays and glows in UV light
- High refractive index (2.45)
- Chemically inert (as each C is sp^3 hybridised and has no unpaired electron present)
- Giant three-dimensional structure, C–C **(1.54 Å) and bond angle 109.5°**

13. Graphite:
- Soft, greasy, dark greyish coloured cry-stalline solid
- Good conductor of electricity
- Also known as *black lead* or *Plumbago*, as it leaves black mark on paper
- Chemically more active than diamond
- Each C is sp^2 hybridised; C–C (1.42 Å); interlayer distance 3.4 Å
- Thermodynamically more stable form

14. Fullerenes or Buckminsterfullerenes or bucky balls:

[C_{60} fullerene]:
- 12 five-membered rings
- 20 six-membered rings
- Six-membered rings are fused with other six-membered as well as five-membered ring
- Five-membered rings are fused with other six-membered rings only

[C_{70} fullerene]:
- 12 five-membered rings
- 25 six-membered rings
- Six-membered rings are fused with other six-membered as well as five-membered rings
- Five-membered rings are fused with other six-membered rings only

Both C_{60} and C_{70} fullerenes have alternate single and double bonds, similar to the structure of a benzene.

15. Amorphous or microcrystalline forms of carbon:

a. Coke

b. Charcoal—Wood charcoal, animal charcoal (bone black), sugar charcoal, activated charcoal

c. Carbon black or lamp black

16. Tin produces a crackling sound on bending, which is known as *tin cry* or *cry of tin*.

Sn is very brittle and turns into powdered form. This is known as *tin disease* or *tin pest* or *tin plague*. White tin (β-tin) is stable at room temperature and transform into grey tin (α-tin) at 268 K.

17. Non-oxidising acids do not attack C and Si.

Sn dissolves slowly in dil HCl but readily in conc HCl.

Pb dissolves in HCl forming insoluble $PbCl_2$, which is soluble in hot water.

Ge is not attacked by dil HCl; but on heating Ge metal in HCl gas, $GeHCl_3$ (germanium chloroform) is formed. Conc HNO_3 attacks Ge, Sn and Pb.

18. Except carbon, Si, Ge, Sn and Pb dissolve in aqueous NaOH to evolve H_2.

$$M + 2NaOH + H_2O \longrightarrow Na_2MO_3 + 2H_2\uparrow$$

19. Oxides of carbon: – **CO, CO_2, C_3O_2**

[CO or $:C \equiv \ddot{O}$]:
- Colourless, odourless gas.
- Neutral oxide and sightly soluble in water.
- Combustible but does not support combustion.
- Poisonous gas; combines irreversibly with haemoglobin in red blood cells to form carboxyhaemoglobin, which is 300 times more stable than oxyhaemoglobin. Thus, haemoglobin no longer acts as an oxygen carrier.

$$Hb + O_2 \rightleftharpoons \underset{\text{(Oxyhaemoglobin)}}{Hb\text{–}O_2}$$

$$Hb + CO \longrightarrow \underset{\text{(Carboxyhaemoglobin)}}{Hb\text{–}CO}$$

[CO_2 or $O=C=O$]:
- Used as fuel in the form of water gas ($CO + H_2$) and producer gas ($CO + N_2$)
- Colourless, odourless and tasteless gas.
- Slightly soluble in water, acidic oxide.
- 1.5 times heavier than air.

- Solid CO_2, i.e. dry ice is used as a refrig-erant and is known as Drikold or Cardice.
- Neither combustible nor a supporter of combustion.
- Carbogen (i.e. 95% O_2 and 5% CO_2) is used for artificial respiration.
- Used as fire extinguisher.
- Foul smelling gas.

C_3O_2 or $O=C=C=C=O$

20. **Carbides:** These are binary compounds in which carbon combines with more electropositive elements than itself (except hydrogen).

Classification of carbides:

a. **Ionic or salt-like carbides:** Formed by highly electropositive elements of groups 1, 2, 13 (except B), coinage metals, Zn, Cd and some lanthanides. These are further classified into:

i. **Acetylides:** Contain $(C \equiv C)^{2-}$ ion and give acetylene on hydrolysis, e.g. BaC_2, CaC_2.

ii. **Methanides:** Contain C^{4-} ion and liberate methane on hydrolysis, e.g. Al_4C_3, BeC_2.

iii. **Allylides:** Contain C_3^{4-} ion and give propyne or allylene on hydrolysis, e.g. Mg_2C_3.

b. **Covalent carbides:** Formed by metalloids, e.g. B_4C and SiC.

c. **Metallic or interstitial carbides:** Formed by transition elements. Carbon being small occupies the interstitial position in the metal lattice.

21. **Fuel:** It is any combustible substance which on burning produces heat energy without the production of undesirable product.

Different types of fuel:

a. **Solid fuels:** Wood, coal, coke, charcoal etc.

b. **Liquid fuels:** Petroleum products, e.g. petrol, kerosene etc.

c. **Gaseous fuels:**

i. Water gas—Mainly consists of CO and H_2

ii. Coal gas—Mixture of CH_4, CO, C_2H_4, C_2H_2, CO_2, N_2 etc.

iii. Producer gas—CO and N_2

iv. Oil gas—Mixture of lower hydrocarbons CH_4, C_2H_4, C_2H_2 etc.

v. Natural gas—Mainly CH_4

vi. LPG—Mixture of butane and isobutane

vii. Biogas—Mainly CH_4

22. **Calcium cyanamide:** CaNCN, commonly known as *Nitrolim*, acts as a good nitrogenous fertiliser. When added to soil, it first changes into $CaCO_3$ and cyanamide.

$$CaNCN + CO_2 + H_2O \longrightarrow CaCO_3 + \underset{\text{Cyanamide}}{H_2N{\cdot}CN}$$

Cyanamide hydrolyses in two steps to give ammonia, NH_3.

$$H_2N{\cdot}CN + H_2O \longrightarrow \underset{\text{Urea}}{H_2NCONH_2}$$

$$H_2NCONH_2 + H_2O \longrightarrow CO_2\uparrow + \underset{\text{Ammonia}}{2NH_3}$$

Ammonia is converted into nitrates by nitrifying bacteria. On account of its slow conversion into ammonia and nitrates, CaNCN is a valuable fertiliser as its effects are of prolonged nature.

23. **Silicates:** These are metal derivatives of silicic acid, $Si(OH)_4$ or H_4SiO_4. Silicates are formed by heating metal oxide or carbonate with silica. The basic unit of silicates is SiO_4^{4-} (tetrahedron).

Classification of silicates:

Type	No. of oxygen atom shared per SiO_4^{4-} unit	General formula of basic unit	Example
a. Orthosilicate	None	SiO_4^{4-}	Phenacite, Be_2SiO_4
b. Pyrosilicate	1	$Si_2O_7^{6-}$	Thortveitite, $Sc_2[Si_2O_7]$
c. Cyclic silicates	2	$(SiO_3^{2-})_n$	Benoitoite, $BaTiSi_3O_9$
d.	Infinite chain silicates		
i. Pyroxenes or metasilicates (single chain)	2	$(SiO_3)_n^{2n-}$	Spodumene, $LiAl(SiO_3)_3$
ii. Amphiboles or meta tetrasilicates (double chain)		$(Si_4O_{11})_n^{6n-}$ $(Si_4O_{11})_2$	Temolite, $[Ca_2Mg_5(OH)_2]$
e. Two-dimensional sheet silicates	3	$(Si_2O_5)_n^{2n-}$	Mica, clay
f. Three-dimensional sheet silicates or framework minerals	4	$(SiO_2)_n$	Quartz, tridymite etc.

24. **Zeolites:** These are widely used as ion exchangers and are represented by the general formula

$$M_{x/n}[(AlO_2)_x (SiO_2)_y]{\cdot}zH_2O$$

where M is the metal cations, such as $Na^{\oplus}$, $K^{\oplus}$ or Ca^{2+}; *n* is charge on metal ion; and *z* is the number of moles of water molecules of crystallisation.

25. **Sodium silicate (Na_2SiO_3):** It is also known as water glass and is chemically sodium metasilicate containing an excess of silica. Its composition may vary from $Na_2SiO_3{\cdot}SiO_2$ to $Na_2SiO_3{\cdot}3SiO_2$.

26. When in a solution of sodium silicate ($\rho = 1.1$ g cm^{-3}), some coloured metal salts such as cobalt nitrate or nickel chloride are placed and the whole solution is left as such overnight, beautiful hollow tubes of metallic silicate gel possessing different colours shoot up from these crystals, which look like plants. This is known as *silica garden.*

27. **Silicones:** • Organosilicon polymers.
   - General formula $(R_2SiO)_x$ (where R= alkyl or aryl group).
   - Contain Si–O–Si linkage.
   - Synthesised by hydrolysis of aryl or alkyl substituted silicon halides followed by condensation.
   - These are stable towards heat and inert towards chemical reagents.
   - Good chemical insulators
   - Non-toxic and water repellents.
   - Used in silicon therapy and cosmetic surgery.

28. **Glass:** It is a translucent or transparent amorphous supercooled solid solution of silicates and borates. Glass is not a true chemical compound as its composition is variable. Ordinary glass can be represented by an approximate formula: $R_2O{\cdot}MO{\cdot}6SiO_2$, where R = Na or K; M = Ca, Ba, Pb or Zn.

29. **Etching of glass:** Glass is attacked by HF; this property is used in etching of glass.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

30. **Some important terms:**

Common name	Chemical name	Chemical formula
Nitrolim	Calcium cyanamide	CaNCN
Carborundum	Silicon carbide	SiC
Water glass	Sodium silicate	Na_2SiO_3
Tin salt	Hydrated stannous chloride	$SnCl_2{\cdot}2H_2O$
Butter of tin or oxymuriate of tin	Stannic chloride pentahydrate	$SnCl_4{\cdot}5H_2O$
Litharge	Crystalline lead monoxide	PbO
Massicot	Powdered lead monoxide	PbO
Red lead or minium or *sindoor*	Lead oxide	Pb_3O_4 or $2PbO{\cdot}PbO_2$
Sugar of lead white lead	Lead acetate [basic lead carbonate]	$(CH_3COO)_2Pb$ $PbCO_3Pb(OH)_2$
Chrome yellow	Lead chromate	$PbCrO_4$
Chrome red	Basic lead chromate	$PbCrO_4{\cdot}PbO$

31. **Germanium:** It is used in IR prisms and lenses.

32. SiC is called *carborundum.* It is hard and refractory material which is used as an abrasive.

33. **a.** β-tin or white tin is not attacked by air or water at ordinary temperature, but on heating with air or oxygen forms SnO_2.
   b. β-tin is not attacked by dil HCl or H_2SO_4 but dissolves in conc HCl or H_2SO_4 to yield $SnCl_2$ and $SnSO_4$, respectively.
   c. With hot alkali, it forms stannates $[Sn(OH)_6]^{2-}$.

34. Lead (Pb) when exposed to air gets covered with a thin layer of $Pb(OH)_2$ and $PbCO_3$. With conc H_2SO_4, insoluble coating of $PbSO_4$ is formed, which protects lead from further reacting with the acid.

35. Three crystalline forms of SiO_2 are quartz, tridymite and cristobalite. Quartz is used as piezoelectric crystal.

36. SiO_2 is acidic, GeO_2 and SnO_2 are amphoteric, and PbO_2 is basic.

37. SnO_2 is prepared by heating Sn with air or conc HNO_3. It is used as polishing powder and in the manufacture of glass and pottery.

38. Pb_3O_4 is called red lead or *sindoor* and is a combination of $2PbO{\cdot}PbO_2$.

39. **Oil dag:** It is a colloidal graphite solution in oil. It protects against corrosion.

40. **Aqua dag:** It is a colloidal suspension of fine particle of graphite in water, used as a lubricant. It forms a smooth continuous dry film with extra long wear life.

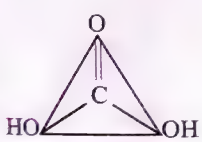
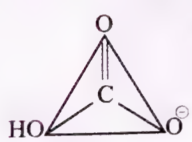
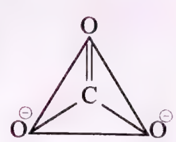
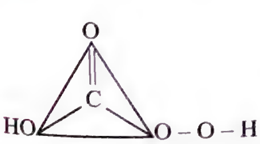
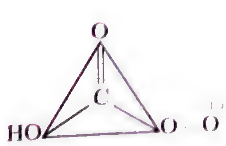
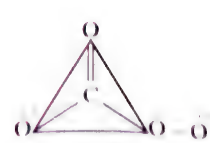
41. Sn has maximum number of 10 istopes.

42. 1 carat of diamond = 0.2 g (200 mg).

43. 1 B.T.U. (British Thermal unit) = 252 calories.

Hybridisation, Geometry and shape of some compounds of Group 14 (4 e^-) elements

Symbols used : SN = Steric number, lp = Lone pair, bp = bond pair, H = Hybridisation, G = Geometry, S = Shape T.H = Tetrahedron, Tbp = Trigonal bipyramid, O.H = Octahedral, Pbp = Pentagonal bipyramid, T.E = Transition elements, C.N. = Coordination number, V = No. of valence e^-'s, M = No. of monovalent attached to central atom, O.S. = oxidation state., (e) = equatorial bond, (a) = axial bond

1. CO_2	$O=C=O$ ($\mu = 0$)	(Note π-bond are excluded from hybridisation)	
$H = \frac{1}{2}(V+M) = \frac{1}{2}(4+0) = 2$		SN = $2bp$, $H = sp$, Geometry = linear, 180°	
2. $:C \equiv O$ ($\mu \neq 0$)	SN = $1bp + 1lp = 2$	$H \Rightarrow sp$, $H = \frac{1}{2}(V+M)$ $= \frac{1}{2}(4+0) = 2$	Geometry = linear, 180°
3. H_2CO_3 (Carbonic acid) (O.S. = +4) (diabasic acid)		**Note:** Ions of acids and per acids have same hybridisation at the central atom.	
H_2CO_3 (Carbonic acid) $HO-\overset{\overset{O}{\|\|}}{C}-OH$ (a) $H = \frac{1}{2}(V+M) = \frac{1}{2}(4+2) = 3$  (a) $\mu \neq 0$	$HCO_3^{\ominus}$ (Bicarbonate ion) $HO-\overset{\overset{O}{\|\|}}{C}-O^{\ominus}$ (b) SN = $3bp$  (b) $\mu \neq 0$	CO_3^{2-} (Carbonate ion) $^{\ominus}O-\overset{\overset{O}{\|\|}}{C}-O^{\ominus}$ (c) $H = sp^2$  (c) $\mu = 0$	[C-atom does not have d-orbitals so one ($p\pi-p\pi$) multiple bond] Geometry = Planar, 120° (Due to three equivalent resonance structures)
4. H_2CO_4.(O.S = + 4) (Peroxy carbonic acid) or (Percarbonic acid) $HO-\overset{\overset{O}{\|\|}}{C}-O-O-H$ (a) $H = \frac{1}{2}(V+M) = \frac{1}{2}(4+2) = 3$  (a) $\mu \neq 0$	$HCO_4^{\ominus}$ (Peroxy bicarbonate ion) $HO-\overset{\overset{O}{\|\|}}{C}-O-O^{\ominus}$ (b) SN = $3bp$  (b) $\mu \neq 0$	CO_4^{2-} (Peroxy carbonate ion) or (Peroxo-carbonate ion) or (Percarbonate ion) $^{\ominus}O-\overset{\overset{O}{\|\|}}{C}-O-O^{\ominus}$ (c) $H = sp^2$  (c) $\mu \neq 0$	[C-atom does not have d-orbitals, so one ($p\pi-p\pi$) multiple bond] Geometry = Planar, 120°

7.1 INTRODUCTION

Group 14 consists of carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). As in group 13 elements, in this group also there is a discontinuity in general properties between the elements. Carbon is strictly non-metallic, silicon is essentially a non-metal in its chemical properties, germanium is a metalloid, i.e. a semi-metal with pronounced metallic character, whereas tin and lead are metallic in nature. Carbon is an essential constituent of all organic matter, whereas silicon is the main constituent of inorganic matter.

7.2 ABUNDANCE AND OCCURRENCE

Carbon is the seventeenth most abundant element by mass in the earth's crust. Carbon is widely distributed in nature in free or native state as well as in combined state. In the native state, it occurs in the form of coal, graphite and diamond. In the combined state, it is present as carbohydrates, hydrocarbons, CO_2 gas, metal carbonates etc. Carbon is the most versatile element in the world. In combination with other elements such as dihydrogen, dioxygen, sulphur and chlorine, it provides an astonishing array of materials ranging from living tissues to drugs and plastics. Organic chemistry is devoted to carbon containing compounds. Carbon is an essential constituent of all living organisms.

Naturally occurring carbon contains two stable isotopes, $^{12}_{6}C$ (98.9%) and $^{13}_{6}C$ (1.1%), in addition to traces of the radioactive $^{14}_{6}C$ isotope. The isotope ^{14}C has a half life of 5770 years and is used in radiocarbon dating to determine the age of archaeological specimens of organic origin. The isotope ^{12}C is the international standard for atomic mass measurement and assigned a mass of 12.00000 units.

Silicon is the second (27.7% by mass) most abundant element (next to oxygen) in the earth's crust. It is present in nature as silica, i.e. SiO_2 (sand and quartz) and silicates. It is an important component of glass, cement and ceramics.

Germanium exists only in traces (1.5 ppm) and is mainly recovered from flue dusts arising from the roasting of zinc ores.

The natural occurrence of tin and lead are 2 ppm and 13 ppm, respectively. Tin mainly occurs as cassiterite or tinstone, SnO_2. The principal ore of lead is galena (PbS), which is often associated with zinc blende, ZnS. Some other ores of lead are cerussite, $PbCO_3$, and anglesite, $PbSO_4$.

7.3 GENERAL TRENDS IN ATOMIC AND PHYSICAL PROPERTIES

Some important atomic and physical properties of group 14 elements are mentioned in Table 7.1.

Table 7.1 Some atomic and physical properties of group 14 elements

Property	Elements				
	Carbon	Silicon	Germanium	Tin	Lead
Symbol	C	Si	Ge	Sn	Pb
Atomic number	6	14	32	50	82
Atomic mass	12.01	28.09	72.60	118.71	207.20
Electronic configuration	$[He]2s^2\,2p^2$	$[Ne]3s^2\,3p^2$	$[Ar]3d^{10}\,4s^2 4p^2$	$[Kr]4d^{10}\,5s^2 5p^2$	$[Xe]4f^{14}\,5d^{10}\,6s^2 6p^2$
Radii (pm) Covalent[a]	77	118	122	140	146
Ionic, M^{4+}[b]	–	40	53	69	78
Ionic, M^{2+}[b]	–	–	73	118	119
Ionisation enthalpy ($kJ\ mol^{-1}$)					
IE_1	1086	786	761	708	715
IE_2	2352	1577	1537	1411	1450
IE_3	4620	3228	3300	2942	3081
IE_4	6220	4354	4409	3929	4082
Electronegativity[c]	2.5	1.8	1.8	1.8	1.9
Density[d] ($g\ cm^{-3}$)	3.51[e]	2.34	5.32	7.26[f]	11.34
Melting point (K)	4373	1693	1218	505	600
Boiling Point (K)	–	3550	3123	2896	2024
Electrical resistivity (Ohm-cm, 293 K)	10^{14}–10^{16}	50	50	10^{-5}	2×10^{-5}

a. For M^{IV} oxidation state. **b.** 6 coordination. **c.** Pauling scale. **d.** 293 K.
e. For diamond, for graphite, density is 2.22. **f.** β-form (stable at room temperature).

7.3.1 Electronic Configuration

The valence shell electronic configuration of group 14 elements is ns^2np^2. However, there is an important difference between the complete electronic configuration of carbon and silicon and those of germanium, tin and lead. Carbon and silicon have a noble gas core beneath the valence shell, whereas germanium and tin have fully filled d^{10} core ($3d^{10}$ and $4d^{10}$, respectively) in-between the noble gas core and valence shell; lead has fully filled $4f^{14}$ and $5d^{10}$ core present in-between the noble gas core and the valence shell. This difference in electronic configuration influences the other properties and consequently the chemistry of all the elements of this group. The electronic configuration of the elements of group 14 is given in Table 7.2.

Table 7.2 Electronic configuration

Element	Electronic configuration
Carbon (C) (Z = 6)	[He] $2s^2\ 2p^2$
Silicon (Si) (Z = 14)	[Ne] $3s^2\ 3p^2$
Germanium (Ge) = 32)	[Ar] $3d^{10}\ 4s^2 4p^2$
Tin (Sn) (Z = 50)	[Kr] $4d^{10}\ 5s^2\ 5p^2$
Lead (Pb) (Z = 82)	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$

7.3.2 Covalent Radii

Statement: The covalent radii of group 14 elements are less than the corresponding group 13 elements.

Explanation: On moving from group 13 to group 14 within the same period, the effective nuclear charge increases and consequently the forces of attraction between the nucleus and the electrons increases, thereby decreasing the covalent radii.

Statement: In group 14 elements, there is a considerable increase in the covalent radius from C to Si; thereafter, from Si to Pb, a small increase in radius is observed.

Explanation: This is due to the addition of a new shell in each succeeding element. The increase in radii from Si to Pb is small due to ineffective shielding of the valence shell electrons by the intervening fully filled lesser shielding *d*- and/or *f*-orbitals.

7.3.3 Ionisation Enthalpy

Statement: The first ionisation enthalpy of group 14 elements are higher than the corresponding group 13 elements.

Explanation: This is due to smaller size of atoms and hence greater effective nuclear charge of group 14 elements as compared to group 13 elements.

Statement: Down the group (↓), the first ionisation enthalpy decreases. There is a sharp decrease from C to Si, whereas from Pb to Sn, there is a slight increase.

$$C > Si > Ge > \underbrace{Pb > Sn}_{\text{Exception}}$$

Explanation: A decrease in the first ionisation enthalpy from C to Sn is due to increase in atomic size and shielding effect of the intervening electrons (i.e. the electrons present in-between the nucleus and valence shell electrons) which overcomes the effect of increased nuclear charge.

An increase in the first ionisation enthalpy from Sn to Pb is because the effect of increased nuclear charge overcomes the shielding effect caused by the presence of fully filled lesser shielding $4f^{14}$ and $5d^{10}$ orbitals in Pb.

7.3.4 Electronegativity

Elements of group 14 are more electronegative than the corresponding group 13 elements due to their small size.

The electronegativity, however, decreases from C to Si and remains constant from Si to Sn and then slightly increases for Pb. This is due to filling of *d*-orbitals in Ge and Sn and both *d*- and *f*-orbitals in Pb.

7.3.5 Physical Properties

7.3.5.1 Metallic Character

All group 14 elements are solids. As compared to group 13 elements, these are less electropositive and hence less metallic. This is because of smaller atomic size and higher ionisation enthalpy.

Down the group (↓), metallic character increases, i.e. C and Si are non-metals, Ge is metalloid, whereas Sn and Pb are soft metals with low melting points. The change from non-metallic to metallic character is due to less effective nuclear charge and increased number of available orbitals, with increase in the size of the atom.

7.3.5.2 Melting and Boiling Points

Statement: The melting and boiling points of group 14 elements are much higher than those of corresponding group 13 elements.

Explanation: This is because group 14 elements form four covalent bonds with each other; hence, there exist strong binding forces between their atoms in the solid as well as in the liquid states.

Statement: The melting and boiling points decrease down the group (↓).

Explanation: This is due to corresponding decrease in the interatomic forces of attraction down the group (↓).

However, the melting point of tin is lower than that of lead.

Carbon has an extremely high melting point (4373 K). As cpmpared to carbon, silicon melts (1693 K) at appreciably lower temperature, but the values of silicon and germanium (1218 K) are still high. This is because they have a very stable diamond-like structure in which smaller atoms are closely packed. Tin and lead are metallic and have more lower melting points (Sn, 505 K; Pb, 600 K) because the M–M bonds are weaker. They do not use all the four valence shell electrons for metallic bonding.

The boiling point of carbon is exceedingly high. It decreases in silicon and then increases in germanium. However, the boiling points decreases from germanium to lead.

7.4 CHEMICAL PROPERTIES

7.4.1 Oxidation States and Chemical Reactivity

The general valence shell electronic configuration of group 14 elements is $ns^2\ np^2$ (where *n* is the number of outermost principal

shell). These elements can attain inert gas configuration either by losing or by gaining four electrons, thereby forming M^{4+} or M^{4-} ion, respectively.

The C^{4+} ion does not exist due to the following reasons:

1. The high sum total of the first four ionisation enthalpies (i.e. $IE_1 + IE_2 + IE_3 + IE_4$) is not compensated by the energy released during compound formation.
2. C^{4+} ion due to its very high charge/radius ratio will polarise the anion appreciably, resulting in the compound being covalent.

The C^{4-} ion does not exist by the addition of four electrons to C to form C^{4-} ion, which is energetically unfavourable. This is because the chemical species has a high charge and thus requires a large amount of energy for adding four electrons.

However, carbon forms carbide (C^{4-}), acetylide (C_2^{2-}) and allyide (C_3^{4-}) ions in methanides, acetylides and allylides, which are ionic carbides. The structure of C_2^{2-} and C_3^{4-} ions are $[\ddot{C} \equiv \ddot{C}]^{2-}$ and $[:\ddot{C} = C = \ddot{C}:]^{4-}$, respectively.

Example of carbides containing C^{4-}, C_2^{2-} and C_3^{4-} ions are (Al_4C_3 and Be_2C), CaC_2 and Mg_2C_3, respectively.

7.4.1.1 Oxidising and Reducing Property

Ge, Sn and Pb can show two different oxidation states, i.e. +2 and +4. These elements in +4 oxidation state behave as oxidising agent, whereas in +2 oxidation state behave as reducing agent.

Oxidising agent: $M^{4+} + 2e^{\ominus} \longrightarrow M^{2+}$

Reducing agent: $M^{2+} \longrightarrow M^{4+} + 2e^{\ominus}$

The stability of +4 oxidation state decreases down the group; hence, Ge(IV) salts are more stable as compared to Pb(IV), i.e. oxidising character increases from Ge(IV) to Pb(IV) salts. Lead tetracetate [$Pb(CH_3COO)_4$] and lead(IV) oxide (PbO_2) are widely used as oxidising agents.

$$\underset{}{Pb(CH_3COO)_4} + \underset{\text{Ethylene glycol}}{\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}} \xrightarrow{\Delta} \underset{\text{Formaldehyde}}{2HCHO} + \underset{\text{Lead acetate}}{Pb(CH_3COO)_2} + \underset{\text{Acetic acid}}{2CH_3COOH}$$

$$\overset{(+4)}{Pb}O_2 + 4H\overset{(-1)}{Cl} \xrightarrow[\text{Conc}]{\Delta} \overset{(+2)}{Pb}Cl_2 + \overset{(0)}{Cl_2} + 2H_2O$$

$$\overset{(+4)}{Pb}O_2 + \overset{(+3)}{Cr}(OH)_3 + 10KOH \longrightarrow 2K_2\overset{(+2)}{Pb}O_2 + 2K_2\overset{(+6)}{Cr}O_4 + 8H_2O$$

The stability of +2 oxidation state increases from Ge to Pb, which means reducing character decreases from Ge(II) to Pb(II), i.e. Ge(II) salts will behave as the strongest reducing agent and Pb(II) salts the weakest.

Germanium is much less abundant than tin is nature; therefore, Sn(II) salts are widely used as reducing agent. Carbon and silicon exhibits an oxidation state of +4. Ge, Sn and Pb apart from showing the group oxidation state (or higher oxidation state) of +4 also show a lower oxidation state of +2 due to inert pair effect.

Table 7.3 Electronic configuration and oxidation state

Element	Electronic configuration	Oxidation states
C	[He] $2s^2\ 2p^2$	(+4)
Si	[Ne] $3s^2\ 3p^2$	+2, (+4)
Ge	[Ar] $3d^{10}4s^2\ 4p^2$	(+2), (+4)
Sn	[Kr] $4d^{10}\ 5s^2\ 5p^2$	(+2), +4
Pb	[Xe] $4f^{14}5d^{10}\ 6s^2\ 6p^2$	(+2)

Note:
- Si exhibits a less stable oxidation state of +2 in SiO.
- Oxidation state (O.S.) in the circle represents that the elements in that O.S. exist and are more stable.

7.4.1.2 Inert Pair Effect

It is the reluctance of ns^2 electrons to unpair and participitate in chemical bond formation. It arises due to the presence of lesser shielding fully filled *d*- and/or *f*-electrons between the valence shell electrons and the noble gas core (Table 7.3) (shielding effects: $s > p > d > f$).

Inert pair effect, which begins to show at Ge, is an important feature of the chemistry of tin and dominates in case of lead.

Down the group (↓), the number of electrons in *d*- or *f*-orbitals increases and, hence, inert pair effect increases from Ge to Pb. Consequently, the stability of group oxidation state (+4) decreases in the order: Ge > Sn > Pb and that of lower oxidation state (+2) increases in the order: Ge < Sn < Pb.

- $$\underset{\text{Stannous chloride}}{SnCl_2} + \underset{\text{Mercuric chloride}}{2HgCl_2} (\downarrow) \longrightarrow Hg_2Cl_2 + \underset{\text{Stannic chloride}}{SnCl_4}$$

  Or

  $$Sn^{2+} + 2Hg^{2+} \longrightarrow Hg_2^{2+} + Sn^{4+}$$

- $$\underset{\text{Stannous chloride}}{SnCl_2} + \underset{\text{Mercurous chloride}}{Hg_2Cl_2} \longrightarrow \underset{\text{Mercury (grey)}}{2Hg (\downarrow)} + \underset{\text{Stannic chloride}}{SnCl_4}$$

  Or

  $$Sn^{2+} + Hg_2^{2+} \longrightarrow Hg + Sn^{4+}$$

- $$2SnCl_2 + 2I_2 \longrightarrow SnCl_4 + SnI_4$$

Since (+4) oxidation state in Ge in more stable than (+2), Ge(II) salts act as strong reducing agent. However, in lead, (+4) oxidation state is less stable than (+2) oxidation state, i.e. Pb(IV) salts act as strong oxidising agents, as is evident from Table 7.4.

Table 7.4 Standard reduction potentials (V)

Acid solution	Basic solution
Oxidation state	Oxidation state
+4, +2, 0	+4, +2, 0
$Sn^{4+} \xrightarrow{+0.15\,V} Sn^{2+} \xrightarrow{-0.14\,V} Sn$	$[Sn(OH)_6]^{2-} \xrightarrow{-0.90\,V} H_2SnO_2^{\ominus} \xrightarrow{-0.91\,V} Sn$
$PbO_2 \xrightarrow{+1.46\,V} Pb^{2+} \xrightarrow{-0.13\,V} Pb$	$PbO_2 \xrightarrow{+0.28\,V} PbO \xrightarrow{-0.54\,V} Pb$

7.4.1.3 Covalent–Ionic Character

Compounds of group 14 in (+4) oxidation state are expected to form covalent compounds because of their extremely small size and high charge density (i.e. their charge/radius ratio) will be high. Hence, according to Fajans' rule, these compounds will have high polarising ability, i.e. they polarise the electron cloud of the anion to a great extent, thus inducing covalent character in the compound.

Compounds in lower oxidation state (+2) are expected to be ionic; for example, $SnCl_2$ is an ionic solid, and $SnCl_4$ is a covalent liquid.

Pb(II) salts are ionic, stable and more common than Pb(IV) salts. The lower valencies are more ionic than the higher valencies because the radius of M^{2+} is greater than that of M^{4+}. Thus, according to Fajans' rule, the smaller the ion, the greater the tendency to covalency.

7.4.1.4 Four Covalent Bonds

The majority of the compounds formed by group 14 elements have four covalent bonds. This can be explained as follows. In these cases, all the four valence shell electrons participate in bonding. In the valence bond theory (VBT) this is explained by promoting an electron from ns^2 orbital to np orbital.

	2s	2p
C (ground state)	⇅	↑ ↑ □
	Two unpaired electrons, hence only two bonds are formed	
C (excited state)	↑	↑ ↑ ↑

sp^3 hybridisation; tetrahedral geometry. Four unpaired electrons, hence can form four covalent bonds

The energy needed to unpair and promote an electron from ns to np is more than compensated by the energy released during the formation of two extra covalent bonds. The distribution of the four orbitals results in a tetrahedral structure, consistent with sp^3 hybridisation. In the tetravalent state, the number of electrons around the central atom in a molecule is eight.

Being *electron precise* molecule, these are not expected to act as electron acceptor or electron donor species. This is true in case of carbon but not in other cases because carbon does not have vacant d-orbital in its valence shell; it cannot act as electron acceptor or it cannot expand its coordination number beyond 4. In other words, maximum covalency of carbon is 4. However, Si, Ge, Sn and Pb, due to availability of vacant d-orbital in their valence shell, can show a coordination number greater than 4, i.e. 5 and 6, forming pentacoordinated and hexacoordinated complexes. For example, $[SiF_5]^{\ominus}$, $[SiF_6]^{2-}$, $[Sn(OH)_6]^{2-}$ etc.

7.4.1.5 Catenation

Carbon has the remarkable property of **catenation** which may be defined as the ability of like atoms to link with one another through covalent bonds. This is due to smaller size and higher electronegativity of carbon atom. The property of catenation depends upon the strength of elements-element bond. Since the bond energy of C—C bonds is very large (355 kJ mol^{-1}), carbon forms long straight or branched C—C chains or rings of different sizes and shapes. However, as we move down the group, the element-element bond energies decrease rapidly viz. C—C (355 kJ mol^{-1}), Si-Si (200 kJ mol^{-1}), Ge—Ge (167 kJ mol^{-1}) and therefore the tendency for the catenation decreases in the order C >>> Si = Sn >>> Pb.

7.4.1.6 Tendency to Form Multiple Bonds

1. **$p\pi$–$p\pi$ bond:** Carbon has a strong tendency to form $p\pi$–$p\pi$ multiple bonds either with itself (C=C) or (C≡C) or with other elements of similar size (C=O, C=N, C≡N). This is due to small size and high electronegativity of carbon. The extent of overlap which can result in multiple bond formation is maximum in case of C, i.e. in C=C, it is $2p$ orbital of C overlapping sideways with $2p$ orbital of C.

   Down the group (↓), the tendency to form $p\pi$–$p\pi$ bond decreases drastically due to increase in size and decrease in electronegativity of the atom. The interaction of $3p$ orbital of silicon and $2p$ orbital of atom of the second row element (carbon, nitrogen, oxygen) will result in much poor overlap and hence a weaker bond. In confirmation of this it is observed that:

   a. Silicon does not form any compound analogous to ethylene, acetylene, benzene, graphite etc.

   b. CO_2 is a gas, and SiO_2 is a high melting solid.

2. **$p\pi$–$d\pi$ bond:** Because carbon does not have d-orbital in its valence shell, it does not form $p\pi$–$d\pi$ bond, but other elements of group 14 have vacant d-orbital in their valence shell and hence have a tendency to form $p\pi$–$d\pi$ bond. This tendency is particularly strong in case of Si linked

to O and N. For example, trimethylamine, $(CH_3)_3N$, is pyramidal and acts as a Lewis base, whereas trisilylamine, $(SiH_3)_3N$, is planar and has very little basic character.

Compounds $(CH_3)_3N$ and $(SiH_3)_3N$ have similar formula but have totally different structures. In trimethylamine, $(CH_3)_3N$, N is sp^3 hybridised with one lone pair. The geometry is tetrahedral. However, as one of the sp^3-hybridised orbital is occupied by lone pair of electron, $(CH_3)_3N$ has a pyramidal shape.

Since lone pair has got a directional character in $(CH_3)_3N$, it behaves as a Lewis base. However, in trisilylamine, $(SiH_3)_3N$, N is sp^2 hybridised and the lone pair of electron occupies $2p$ orbital on N. The three sp^2 orbitals are used for σ bonding, giving a planar triangular structure, and the lone pair of electrons occupies a p-orbital at right angle to the plane triangle.

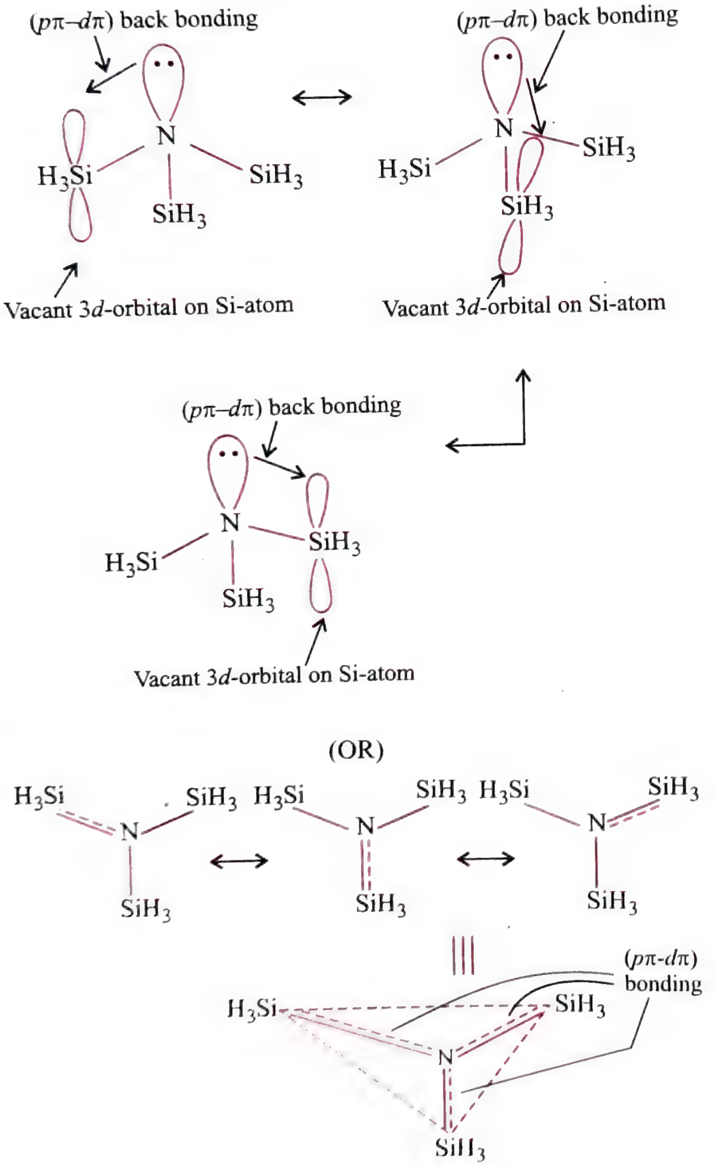


Fig. 7.1 $(SiH_3)_3N$; planar triangular structure

This filled $2p$ orbital on N overlaps with the vacant $3d$ orbital on each of the three silicon atoms and results in π bonding, more accurately $p\pi$–$d\pi$ bonding (Fig. 7.2) because it is from filled p-orbital to an empty d-orbital. This results in shortening of N–Si bond lengths. Since N no longer has a lone pair of electrons, the molecule no longer has donor properties, that is why $(SiH_3)_3N$ has very little basic character. Similar $p\pi$–$d\pi$ bonding is impossible in $(CH_3)_3N$ because C does not possess d-orbitals; hence, it is pyramidal.

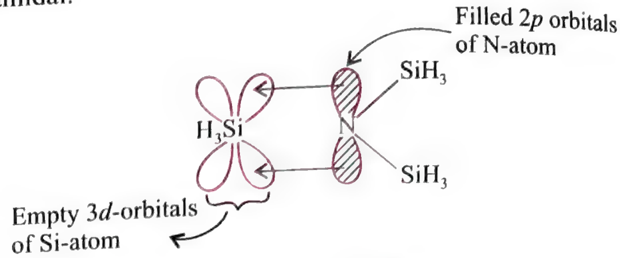


Fig. 7.2 $p\pi$–$d\pi$ bonding

7.4.1.7 Reactivity Towards Oxygen

All group 14 elements, on heating with oxygen, forms oxides. These are mainly of two types: monoxides (MO) and dioxide (MO_2).

SiO exists only at high temperature where it is assumed to be formed by the reduction of SiO_2 with Si:

$$SiO_2 + Si \longrightarrow 2SiO$$

7.4.1.8 Reactivity Towards Water

Carbon, silicon and germanium do not decompose water at all. However, on red heating, these elements, except lead, decompose steam.

$$C_{(s)} + \underset{\text{Steam}}{H_2O} \xrightarrow{\text{Red heat}} CO\uparrow + H_2\uparrow_{(g)}$$

$$Si_{(s)} + \underset{\text{Steam}}{2\,H_2O} \xrightarrow{\text{Red heat}} SiO_{2(s)} + 2H_2\uparrow_{(g)}$$

$$Sn_{(s)} + \underset{\text{Steam}}{2H_2O} \xrightarrow{\text{Red heat}} SnO_{2\,(s)} + 2H_2\uparrow_{(g)}$$

Lead is not attacked by pure air free water (except at the boiling point). It is readily corroded by water containing dissolved air, forming lead hydroxide which is appreciably soluble in water. The solvent action of water is known as *plumbosolvency*.

$$2Pb + 2H_2O + O_2 \longrightarrow 2Pb\,(OH)_2$$

7.5 GENERAL CHARACTERISTICS OF THE COMPOUNDS OF GROUP 14 ELEMENTS

7.5.1 Hydrides

All group 14 elements form covalent hydrides directly or indirectly. The number of state hydrides and ease with which these are formed decreases from C to Pb. This is due to decrease in catenating ability from C to Pb, with the decrease in M–M bond strength.

Carbon forms a large number of chain and ring compounds.

1. Alkanes (paraffins; general formula: C_nH_{2n+2})
2. Alkenes (olefins; general formula: C_nH_{2n})
3. Alkynes (acetylenes; general formula: C_nH_{2n-2})
4. Aromatic compounds

These are the basis of organic chemistry. Carbon has a strong tendency for catenation (forming chains) due to high bond strength of C–C bond.

Silicon forms a limited number of saturated hydrides, Si_nH_{2n+2}, called silanes.

Compounds of Ge and hydrogen are known as germanium hydrides. These are:

a. Also known as germanes, Ge_nH_{2n+2}, where $n_{max} = 5$.

b. Straight chain compounds.

c. Colourless gases or volatile liquids.

d. Similar to silanes, but are less volatile, less flammable and are unaffected by water or aqueous acids or alkalis.

GeH_4 can be made by the following methods:

i. $GeCl_4 + Li[AlH_4] \xrightarrow{\text{Dry ether}} GeH_4 + LiCl + AlCl_3$

ii. $GeO_2 + Na[BH_4] \xrightarrow[\text{solution}]{\text{Aqueous}} GeH_4 + NaBO_2$

Tin forms:

1. Stannane (SnH_4): It is much less stable.

   a. It can be made by reducing $SnCl_4$ with $Li[AlH_4]$ or $Na[BH_4]$.

   $SnCl_4 + Li[AlH_4] \longrightarrow SnH_4 + LiCl + AlCl_3$

   b. It acts as a strong reducing agent.

   c. It is unaffected by water and dilute acids and alkalis, but it reacts slowly with concentrated solutions.

2. Distannane, Sn_2H_6, is known and is even less stable. No higher stannanes are known.

   Lead forms plumbane, PbH_4, which is even less stable and even more difficult to prepare. The preparative methods for other hydrides fail. It has been prepared in traces and at low concentrations by cathodic reduction and detected using a mass spectrometer.

   In general, it may be concluded that the stabitily of the hydrides of group 14 elements decrease down the group (↓) from C to Pb. Since thermal stability decreases, their tendency to act as reducing agent increases down the group (↓).

7.5.2 Oxides

1. All elements of group 14 on heating with oxygen form mainly two types of oxides: monoxide, MO (CO, SiO, GeO, SnO, PbO) and dioxide, MO_2 (CO_2, SiO_2, GeO_2, SnO_2 and PbO_2). Lead also forms an oxide Pb_3O_4, which is a mixed oxide of PbO and PbO_2, viz. $2PbO{\cdot}PbO_2$.

2. **Monoxides, MO:** Carbon monoxide, CO.

   Other monoxides can be prepared as follows:

   SiO: $SiO_2 + Si \xrightarrow[\text{Vacuum}]{1300°C} 2SiO$

   GeO: Dehydrate $Ge(OH)_2$

   $Ge(OH)_2 \xrightarrow{\Delta} GeO + H_2O$

   or $GeO_2 + Ge \xrightarrow{1000°C} 2GeO$

   SnO: $Sn(OH)_2 \xrightarrow[\text{In absence of air}]{\Delta} SnO + H_2O$ (dehydration)

   PbO: $\underset{\text{Molten}}{2Pb} + \underset{\text{(Air)}}{O_2} \xrightarrow{>600°C} PbO$

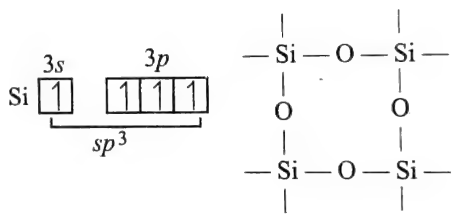
   (For details, refer to Section 7.15.15)

   Among monoxides, CO is neutral, GeO is basic, while SnO and PbO are amphoteric.

3. **Dioxides, MO_2:** CO_2 is a gas, whereas SiO_2 is a high melting solid. This can be explained on the basis of difference in the structures of CO_2 and SiO_2. In CO_2, C is *sp* hybridised.

4. The formation of double bond between C and O atoms requires the lateral overlap between 2*p* orbital of C atom with 2*p* orbital of O atom. Since the size and energy of 2*p* (C) and 2*p* (O) are nearly of the same level, they overlap effectively to form π bond between C and O. This permits the formation of CO_2 molecule.

   In SiO_2, Si is sp^3 hybridised, each Si atom is bonded to four oxygen atoms which are arranged tetrahedrally around Si and each O atom is covalently bonded to two Si atoms. This gives rise to three-dimensional structure for SiO_2. The bond strength of Si–O is very high; thus, SiO_2 has a high melting point.



The characteristic difference between CO_2 and SiO_2 can be explained as follows. The carbon atom has a small radius, the positively charged nucleus, therefore, attracts the outer electrons very strongly and does not permit the oxygen to combine with another carbon atom. In silica, SiO_2, however, the size of Si atom is fairly large as compared to that of carbon. As a result, the positively charged carbon nucleus cannot attract the outer electrons so strongly; hence, the oxygen can be shared between two different silicon atoms. This leads to the formation of giant SiO_2 molecule, but not a giant CO_2 molecule.

SiO_2 cannot have structure like CO_2, as the lateral overlap between 3*p* orbital of Si and 2*p* orbital of O is not feasible. It is due to the difference in size and energy of the two orbitals. Hence, these orbitals cannot overlap effectively to form π bond between Si and O atom. Thus, O = Si = O does not exist. The tetravalency of Si is achieved by forming four Si–O bonds.

GeO_2 and SnO_2 are obtained by heating Ge and Sn in air:

$Ge + O_2 \longrightarrow GeO_2$

$Sn + O_2 \longrightarrow SnO_2$

PbO_2 is formed by electrolytic oxidation of Pb.

5. **Acid–base character:** Down the group (↓), the acidic character decreases and the basic character increases.

$$\xrightarrow{\text{Acidic character decreases}}$$
$CO_2 \quad SiO_2 \quad GeO_2 \quad SnO_2 \quad PbO_2$
$$\xrightarrow[\text{Basic character increases}]{}$$

CO_2, SiO_2, GeO_2 being acidic reacts with base.

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$
$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$
$$SiO_2 + 2NaOH \longrightarrow \underset{\text{Sodium silicate}}{Na_2SiO_3} + H_2O$$
$$GeO_2 + 2NaOH \longrightarrow \underset{\text{Sodium germanate}}{NaGeO_3} + H_2O$$

In contrast, SnO_2 and PbO_2 being amphoteric react with both acids and bases.

$$SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$$
$$SnO_2 + 2NaOH \longrightarrow \underset{\text{Sodium stannate}}{Na_2SnO_3} + H_2O$$
$$PbO_2 + 4HCl \longrightarrow PbCl_4 + 2H_2O$$
$$PbO_2 + 2NaOH \longrightarrow \underset{\text{Sodium plumbate}}{Na_2PbO_3} + H_2O$$

7.5.2.1 Oxidising Behaviour

Due to inert pair effect, in Pb, +2 oxidation state is more stable as compared to +4 oxidation state. Hence, Pb(IV) compounds behave as strong oxidising agent.

PbO_2 reacts with HNO_3 or H_2SO_4 to evolve O_2 gas:

$$2PbO_2 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + 2H_2O + O_2$$
$$2PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O + O_2$$

7.5.3 Halides

Tetrahalides (MX_4): All elements of group 14 form tetrahalides which are mostly covalent. The central atom of these tetrahalides undergoes sp^3 hybridisation to give a tetrahedral molecule; for example, CF_4.

Among the simple tetrahalides, tetrafluorides of C, Si and Ge (i.e. CF_4, SiF_4 and GeF_4) are gases, whereas the tetrafluorides of Sn and Pb (i.e. SnF_4 and PbF_4) are solids. This is because CF_4, SiF_4, GeF_4 are covalent and, hence, are volatile gases. However, SnF_4 and PbF_4 are ionic in character, have three-dimensional structures and are high melting solids. SnF_4 sublimes at 705°C, and PbF_4 melts at 600°C.

Carbon tetrabromide (CBr_4) is a solid, whereas tetra-bromides of silicon, germanium and tin (i.e. $SnBr_4$, $GeBr_4$ and $SnBr_4$) are liquids. Tetraiodides of the first four elements are solids (i.e. CI_4, SiI_4, GeI_4, SnI_4).

$PbBr_4$ and PbI_4 are not known. The non-existence of $PbBr_4$ and PbI_4 can be due to strong oxidising power of Pb(IV) and strong reducing power of $Br^{\ominus}$ and $I^{\ominus}$ ions as illustrated by the $E^{\ominus}$ values.

$$Pb^{4+} + 2e^{\ominus} \rightleftharpoons Pb^{2+}; \quad E^{\ominus} = +1.8\ V$$
$$Br_2 + 2e^{\ominus} \rightleftharpoons 2Br^{\ominus}; \quad E^{\ominus} = +1.09\ V$$
$$I_2 + 2e^{\ominus} \rightleftharpoons 2I^{\ominus}; \quad E^{\ominus} = +0.54\ V$$

The non-existence of $PbBr_4$ and PbI_4 can also be explained as follows:

1. The Pb–Br or Pb–I bonds formed initially does not liberate enough energy to unpair $6s^2$ electrons and promote one of them to $6p$ orbital; hence, lead cannot form four covalent bonds.
2. Alternatively, the electronegativities of Br and I are not high enough to excite $6s$ electrons to $6p$ orbitals; thus, Pb does not form four covalent bonds.

In general, the stability and ionic character of the halides decreases with

a. Increasing atomic number of group 14 elements, i.e. from C to Pb.
b. Increasing atomic number or size of the halogen, i.e. from F to I.

The elements after C have vacant d-orbitals available in their valence shell and Si–F, Si–Cl and Si–O bonds are stronger than C–F, C–Cl and C–O bonds, respectively. This is due to the donation of electron pair from F, Cl or O to vacant $3d$ orbital of Si, giving rise to $p\pi$–$d\pi$ bonding (Fig. 7.3).

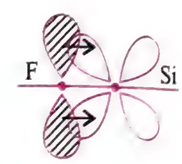


Fig. 7.3 $p\pi$–$d\pi$ bonding in Si–F.

Few important tetrahalides of carbon are as follows:

Tetrafluoromethane, CF_4 (carbon tetrafluoride), is an exceptionally unreactive gas, or highly stable gas.

i. Laboratory method of preparation:
$$CO_2 + SF_4 \longrightarrow CF_4 + SO_2$$
$$SiC + 2F_2 \longrightarrow SiF_4 + CF_4$$
ii. Industrial method of preparation:
$$CF_2Cl_2 + F_2 \longrightarrow CF_4 + Cl_2$$

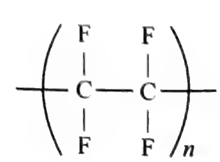
Other fluorine compounds such as hexafluoroethane (C_2F_6) and tetraflouoroethylene (C_2F_4) are known. C_2F_4 polymerises to $(C_2F_4)_n$ under pressure, giving polytetrafluoroethylene or PTFE. Properties of PTFE are as follow:

- Hard, white solid plastic with a greasy feel to touch.
- Much heavier or more dense.
- Good electrical insulator.
- Chemically inert and due to its chemical inertness it is used in the laboratory.
- Expensive.
- Low coefficient of friction.
- Used for coating non-stick pans and razor blades.

Fluorocarbons are useful lubricants, solvents and insulators.

Preparation of PTFE or Teflon (polytetra fluoroethylene)

$$CHCl_3 + HF \xrightarrow[\text{SbFCl}_4\ \text{(Catalyst)}]{SbF_3\ \text{or}} CHF_2Cl \xrightarrow[1070\ K]{\Delta} F_2C=CF_2 + 2HCl$$

$$F_2C=CF_2 \xrightarrow{\text{Pressure}}$$

PTFE

7.5.3.1 Hydrolysis of CCl_4 and $SiCl_4$

Carbon tetrahalides, e.g. CCl_4 does not undergo hydrolysis under normal conditions, whereas silicon tetrahalides undergo hydrolysis easily. This is because carbon does not have vacant d-orbital in its

valence shell and hence cannot coordinate with $\overset{\ominus}{O}H$ ion or water and cannot form five coordinate hydrolysis intermediate.

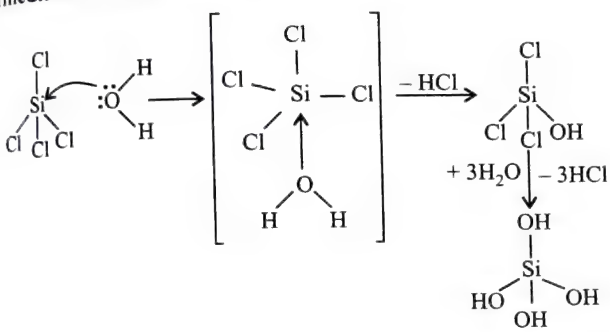
$$CCl_4 + H_2O \longrightarrow \text{No hydrolysis}$$

If sufficient energy is provided by using superheated steam then CCl_4 will hydrolyse:

$$CCl_4 + H_2O \xrightarrow[\text{Steam}]{\text{Superheated}} \underset{\substack{\text{Carbonyl}\\ \text{chloride}\\ \text{(phosgene)}}}{COCl_2} + 2HCl$$

Phosgene is highly toxic and was used as a poisonous gas during World War I.

Silicon tetrahalides, e.g. $SiCl_4$ undergo hydrolysis due to the availability of vacant 3*d*-orbital in the valence shell of Si atom. The reaction occurs by S_N2 mechanism. A lone pair of electron from O of H_2O molecule is donated in the empty 3*d*-orbital of Si, resulting in the formation of a five coordinate hydrolysis intermediate having trigonal bipyramidal structure.



This is followed by the elimination of HCl molecule. The addition of water molecule and elimination of HCl continues till all –Cl groups in $SiCl_4$ are replaced by –OH groups.

Carbon tetrahalides do not form complexes because carbon has no *d*-orbital in its valence shell and cannot expand its coordination number. The tetrahalides of the rest of the elements of group 14, however, do form complexes due to the availability of vacant *d*-orbitals in the valence shell. Hence, these elements can increase their coordination number from 4 to 5 or 6, e.g. $[SiF_6]^{2-}$, $[GeF_6]^{2-}$, $[SnF_6]^{2-}$.

Tetrahalides of Si

Hydrolysis of SiF_4 yields silica and fluorosilicic acid.

$$3SiF_4 + 2H_2O \longrightarrow \underset{\text{Silica}}{SiO_2} + \underset{\text{Fluorosilicic acid}}{2H_2SiF_6}$$

This is because, in case of SiF_4, a secondary reaction occurs between HF and the unchanged SiF_4, forming hexafluorosilicic acid:

$$SiF_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HF$$
$$[2HF + SiF_4 \longrightarrow H_2SiF_6] \times 2$$
$$3SiF_4 + 4H_2O \longrightarrow Si(OH)_4 + H_2SiF_6$$

or

$$SiO_2{\cdot}2H_2O$$

or $3SiF_4 + 2H_2O \longrightarrow SiO_2 + 2H_2SiF_6$

Fluorosilicic acid is known only in solution. It is a strong acid and exists largely in the ionised state.

$$H_2SiF_6 + 2H_2O \longrightarrow 2H_3O^{\oplus} + [SiF_6]^{2-}$$

$[SiF_6]^{2-}$ ion involves sp^3d^2 hybridisation of Si and has an octahedral structure.

SiF_4 is readily hydrolysed by alkali.

$$SiF_4 + 8\overset{\ominus}{O}H \longrightarrow SiO_4^{4-} + 4F^{\ominus} + 4H_2O$$

Other tetrahalides of Si are rapidly hydrolysed by water to give silicic acid.

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{Silicic acid}}{Si(OH)_4} + 4HCl$$

Tetrahalides of Ge, Sn and Pb

Ge(IV) tetrahalides are maximum stable and Pb(IV) tetrahalides are least stable due to inert pair effect. The stability of +4 oxidation states decreases in the order:

Ge(IV) > Sn(IV) > Pb(IV)

The tetrahalides are all colourless, volatile liquids except *GeI_4 and SnI_4, which are bright orange solids.*

7.5.3.2 Charge Transfer Spectra

The orange colour of SnI_4 is caused by the absorption of blue light, the reflected light. Thus, contains mainly high proportion of red and orange. The energy absorbed in this way causes the transfer of an electron from I to Sn. This corresponds to the temporary reduction of Sn(IV) to Sn(III). Since transferring an electron to another atom is transferring a charge, such spectra are called *charge transfer spectra*. This occurs in SnI_4 and GeI_4 because the atoms have similar energy levels. This would be expected because they are close in the periodic table and have similar sizes. Charge transfer spectra do not occur with other halides.

$GeCl_4$ and $GeBr_4$ are hydrolysed less readily. $SnCl_4$ and $PbCl_4$ hydrolyse in dilute solutions, but hydrolysis is often incomplete and can be repressed by the addition of an appropriate halogen acid.

$$Sn(OH)_4 \underset{H_2O}{\overset{HCl}{\rightleftharpoons}} SnCl_4 \underset{H_2O}{\overset{HCl}{\rightleftharpoons}} [SnCl_6]^{2-}$$

Dihalides (MX_2)

Carbon do not form dihalides. The dihalides of Si, Ge, Sn and Pb are known and can be prepared as follows:

$$SiF_4 + Si \rightleftharpoons 2SiF_2$$

$$\underset{\text{Vapour}}{GeX_4} + Fe \xrightarrow{675\text{ K}} 2GeX_2$$

$$Sn + 2HX_{(g)} \longrightarrow SnX_2 + H_2$$

$$Pb^{2+} + 2X^{\ominus} \longrightarrow PbX_2 \ (X = F, Cl, Br, I)$$

The dihalides are much less volatile than tetrahalides and become increasingly powerful reducing agent from Ge to Pb. GeF_2 is a white solid. It has unusual fluorine-brigded polymeric structure, based on a trigonal bipyramid. GeF_3 units share F atoms (giving the formula GeF_2), and Ge also forms a weaker interaction to another F with a lone pair in the fifth position. These units are linked into infinite spiral chains.

$SnCl_2$ in the gaseous phase is angular (Fig. 7.4), with $\angle ClSnCl = 95°$.

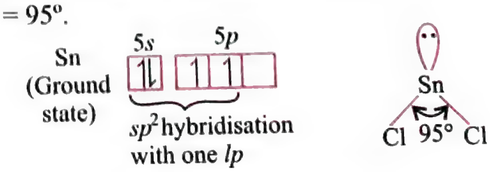


Fig. 7.4 Angular $SnCl_2$ (gas)

Sn is sp^2 hybridised in $SnCl_2$ (gaseous phase) with one of the sp^2-hybridised orbital occupied by the lone pair. The decrease in the bond angle from 120° to 95° is due to greater repulsion between lone pair (*lp*) and bond pair (*bp*) as compared to repulsion between bond pair and bond pair, which leads to contraction in the bond angle.

$SnCl_2$ in the crystalline form has a layer structure with chains of corner-shared trigonal pyramidal $[SnCl_3]$ groups (Fig. 7.5).

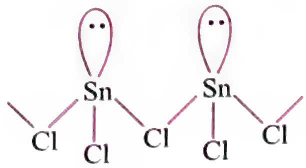


Fig. 7.5 $SnCl_2$ (crystalline)

$PbCl_2$ has a complicated three-dimensional structure. Lead dihalides are fairly insoluble in water. The solubility of $PbCl_2$, $PbBr_2$, PbI_2 increases in the presence of corresponding halogen acid due to the formation of corresponding $[PbX_4]^{2-}$ ion.

$$PbCl_2 + 2Cl^{\ominus} \longrightarrow \underset{\text{Soluble complex}}{[PbCl_4]^{2-}}$$

On dilution, the complex decomposes. The dipositive state in the lead dihalides is stable and shows no reducing property, in contrast to those of Ge and Sn.

7.5.4 Complex Forming Tendency

The ability to form complexes is favoured by

1. High charge
2. Small size
3. Availability of empty orbitals of suitable energy.

Carbon in four covalent compounds contain the maximum of eight electrons. As these structures resemble the structures of noble gas, these compounds are stable and do not behave as electron acceptor; that is why carbon does not form complexes. However, Si, Ge, Sn and Pb, due to availability of vacant *d*-orbital in their valence shell, can accept electron pair, thus expanding their coordination number from 4 to 5 and 6 or, in other words, can form complexes.

$$SiF_4 + 2F^{\ominus} \longrightarrow [SiF_6]^{2-}$$

$$GeF_4 + 2NMe_3 \longrightarrow [F_4Ge{\cdot}(NMe_3)_2]$$

$$SnCl_4 + 2Cl^{\ominus} \longrightarrow [SnCl_6]^{2-}$$

$[SiF_6]^{2-}$ ion can be formed by the reaction between SiO_2 and aqueous HF.

$$SiO_2 + 6HF \longrightarrow 2\overset{\oplus}{H} + [SiF_6]^{2-} + 2H_2O$$

$[SiF_6]^{2-}$ complex is stable in water and alkali, but the others are less stable. $[GeF_6]^{2-}$ and $[SnF_6]^{2-}$ are hydrolysed by alkali, and $[PbF_6]^{2-}$ is hydrolysed both by water and alkali. This is due to decrease in stability of the fluorocomplexes down the group.

$$[SiF_6]^{2-} > [GeF_6]^{2-} > [SnF_6]^{2-} > [PbF_6]^{2-}$$

Ge, Sn and Pb also form chloride complexes such as $[PbCl_6]^{2-}$ and oxalate complexes such as $[Pb(ox)_3]^{2-}$.

7.6 IMPORTANT TRENDS AND ANOMALOUS BEHAVIOUR OF CARBON

Like the first member of other groups, *carbon*, the first member of group 14, also shows anomalous behaviour, i.e. differs from the rest of the members of the family.

The main reasons for these differences are as follows:

1. Exceptionally small atomic and ionic size.
2. Higher electronegativity.
3. Higher ionisation enthalpy.
4. Absence of vacant *d*-orbitals in the valence shell.

The main points of differences are as follows:

1. In carbon, there are only four valence orbitals, i.e. one 2*s* and three 2*p*-orbitals; therefore, it can accommodate only four pairs of electrons around it. Therefore, carbon can have a maximum covalency of four, whereas the other members of group 14, due to the presence of vacant *d*-orbitals in the valence shell, can expand their covalency to *six*. For example, carbon cannot form $[CF_6]^{2-}$, whereas Si forms $[SiF_6]^{2-}$.
2. Carbon has higher melting point and boiling point than the other members of group 14.
3. Due to small size and high electronegativity, carbon has a unique ability to form $p\pi$–$p\pi$ multiple bonds with itself (C = C, C ≡ C) and with other atoms of small size and high electronegativity, e.g oxygen (C = O), nitrogen (C = N, C ≡ N) and sulphur (C = S). The remaining members do not form $p\pi$–$p\pi$ bonds. This is due to decrease in effective overlap which results in the formation of $p\pi$–$p\pi$ bond, which depends on (a) *the size of the orbitals involved* and (b) *the number of non-bonding electrons*.

   a. **Size of the orbitals involved:** In C and other small size, highly electronegative atoms (i.e., N, O, etc.), the orbitals involved in $p\pi$–$p\pi$ bond formation are 2*p*–2*p*. Since the size of these orbitals are small and they are less diffused, the extent of overlap is large and hence $p\pi$–$p\pi$ bond is easily formed.

   Down the group (↓), as the size of the orbitals involved increases, the tendency to form $p\pi$–$p\pi$ bond decreases.

   b. **Number of non-bonding electrons:** The lesser the number of non-bonding electrons, the less will be the repulsion between non-bonding electrons of the atoms involved in $p\pi$–$p\pi$ bond formation and $p\pi$–$p\pi$ bond can be formed.

   Down the group (↓), the number of non-bonding electrons increases, thereby the repulsion between non-bonding electrons of the two atoms involved in bond formation increases, decreasing the extent of overlap and hence the $p\pi$-$p\pi$ bond stability.

   The higher members of group 14 do not form $p\pi$–$p\pi$ bonds, rather they have a tendency to form $d\pi$–$p\pi$ bonds.

Even this tendency to form $d\pi$–$p\pi$ bonds decreases down the group form Si to Pb, as the size of the *d*-orbitals increases.

4. **Catenation:** Carbon is unique among group 14 elements in its ability to catenate. Catenation may be defined as the ability of the atoms of the same elements to link with one another through covalent bonds to form chains and rings. The ability to catenate depends on the strength of elements–elements bond (bond enthalpy). Carbon–carbon bond enthalpy is the largest (348 kJ mol^{-1}); hence, carbon forms long straight or branched C – C chains and rings of different sizes. Down the group (↓), the strength of element–element bond decreases (Table 7.5) rapidly; hence, the tendency for catenation decreases in the order: C >> Si > Ge ≈ Sn.

Table 7.5 Bond enthalpies

Bond	C–C	Si–Si	Ge–Ge	Sn–Sn
Bond enthalpy (kJ mol^{-1})	348	297	260	240

Thermal stability severely limits the maximum number of element–element bonds in straight chain compounds such as hydrides and halides of group 14 elements to 11 or 12 for silicon, 9 or 10 for Ge and only 2 for Sn. Lead does not show catenation ability.

7.6.1 Allotropes of Carbon

The phenomenon by which an element exists in two or more different crystalline or amorphous forms is called *allotropy*, and the different forms are called *allotropic forms or allotropes* of the given element. Different allotropic forms of an element have different physical properties but similar chemical properties.

Cause of allotropy: The phenomenon of allotropy arises due to the following reasons:

1. Difference in the arrangement of atoms or molecules in the crystal lattice, e.g. diamond, graphite and fullerene.
2. Difference in the number of the atoms in the molecule, e.g. O_2 and O_3.
3. Difference in the method of crystallisation.
4. Amount of energy available.

Carbon exists in two allotropic forms:

a. Crystalline
b. Amorphous

Allotropes of carbon

- Crystalline
  - Diamond
  - Graphite
  - Fullerene
- Amorphous
  - Coke
  - Charcoal
  - Carbon black

a. Crystalline allotropic forms of carbon.

i. Diamond

ii. Graphite

iii. Fullerene

These are examples of atomic or covalent crystals.

An atomic or covalent crystal consists of a large network of neutral atoms of the same or different kinds, covalently linked to one another. Hence, covalent crystals are also known as covalent network crystals. A few examples of covalent crystals are diamond, graphite, silicon carbide, boron nitride, silicon dioxide, quartz, rhombic sulphur etc. The valencies in covalent crystals are saturated and covalent bonds are oriented in definite directions. This leads to looser packing and covalent crystals to have open structure as compared to metallic or ionic crystals. However, the covalent bond is very strong; this is why a large amount of energy is required to break it. Covalent crystals are

- Very hard.
- Possess high melting point.
- Possess low volatility.
- Insoluble in most of the solvents.
- Generally bad conductor of electricity (except graphite). This is because these are not made up of ions and do not have free electrons available for electrical conduction, since all the electrons are involved in covalent bond formation.

7.6.1.1 Diamond

Diamond is the purest crystalline allotropic form of carbon.

Occurrence: It occus in nature in the free state. In nature, diamond occurs as octahedral crystals.

Preparation: Artificial diamonds are prepared by heating pure sugar charcoal and iron in a graphite crucible at 3000°C in an electric furnace. At high temperature, carbon dissolves in iron. This molten mass is cooled rapidly by plunging it into molten lead bath and then treated with conc HCl to obtain crystals of artificial diamond. But because of its high cost and poor quality, diamonds are seldom made artificially.

Structure: X-ray studies have shown that crystal of diamond consists of a number of tetrahedral units Fig. 7.6 (a). Each tetrahedral unit contains a carbon atom at the centre, which is linked to other four C-atom placed at the four corners of the tetrahedron. C-atoms of each tetrahedron are also linked by strong C–C covalent bonds with C-atom of each of the neighbouring tetrahedrons Fig. 7.6(b).

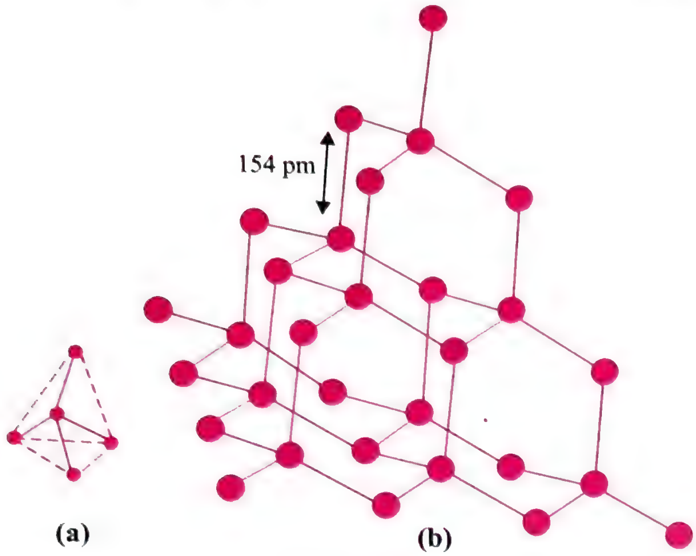


Fig. 7.6 (a) Tetrahedral unit of C-atoms and (b) structure of diamond

Each C-atom is sp^3 *hybridised.* C–C bond distance in diamond is 154 pm, which is a normal distance of C–C covalent bond. As diamond consists of a number of tetrahedral units, it is a giant molecule. Also since each C-atom form four covalent bonds, it produces a repetitive three-dimensional structure using only covalent bonds.

Properties: Diamond exhibits following properties based on its structure:

1. It is the hardest substance known. Due to its great hardness, diamond is used for making glass cutters and rock borers.
2. It has a high melting point. In order to break strong C–C covalent bonds present in diamond, a large amount of energy is required; hence, the melting point of diamond is very high.
3. It has a high relative density (= 3.5).
4. It is transparent to X-rays.
5. It has a high value of refractive index (2.5), which means it can reflect and refract light. It is, therefore, a transparent substance.
6. Since all the four valence shell electrons on each C-atom are used up in making four covalent bonds with other C-atom, therefore the average value of C–C bond order in diamond is one.
7. There is no free electron left in the diamond crystal to carry electricity. Thus, diamond is a bad conductor of electricity. Heat conductivity in non-metals is due to lattice vibrations (photons). So, when diamond is heated, thermal vibrations are rapidly transmitted through diamond, and it acts as a good conductor of heat.
8. It is insoluble in all solvents.
9. At red heat (900°C), diamond burns in air to form CO_2

$$\underset{\text{Diamond}}{C} + O_2 \xrightarrow{900°C} CO_2$$

10. Action of dil H_2SO_4 and $K_2Cr_2O_7$: It is slowly oxidised to CO_2.
11. With Na_2CO_3: On heating with Na_2CO_3, it gives CO.
12. It is stable in vacuum up to 1500°C; but when heated to 1800–2000°C, it is converted into graphite.
13. With F_2: It reacts with F_2 at 700°C to form CF_4.

Uses:

1. For making glass cutter, rock borers and as an abrasive.
2. For making and polishing of hard materials.
3. For making dies for drawing thin wires from metals.
4. For making precious gems and jewellery.

7.6.1.2 Graphite

Like diamond, graphite is also the purest form of carbon. It occurs in nature. It can also be manufactured artificially by heating coke to 3273–3330 K in an electric furnace.

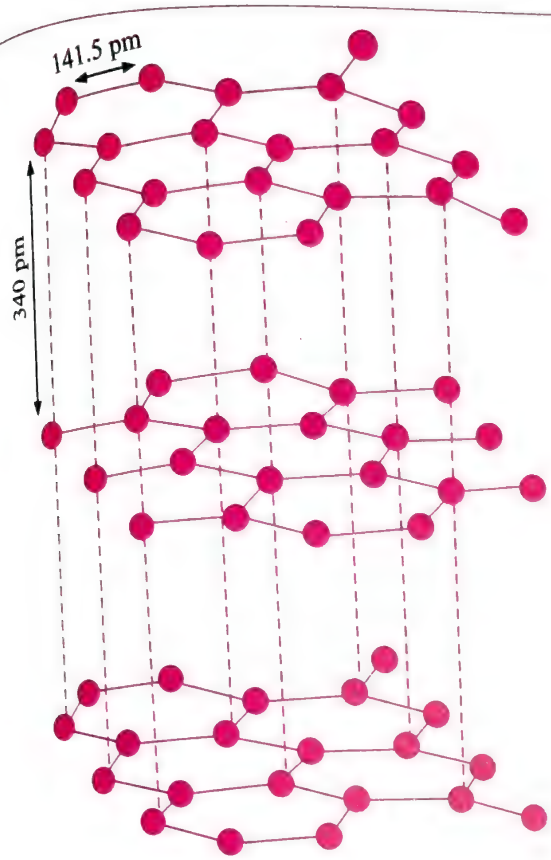
Structure: Graphite is composed of flat two-dimensional sheets or layers of carbon atom. Each sheet or layer consists of flat hexagonal rings of C-atoms [Fig. 7.7(a)] and may be regarded as a fused system of benzene rings [Fig. 7.7(b)]. In each layer, each C-atom is linked to three C-atoms by C–C covalent bond. The C–C bond length in each hexagonal ring is 141.5 pm, as each C-atom is sp^2 hybridised, i.e. only three of the valence electrons of each C-atom are involved in forming σ bond (using sp^2 hybrid orbitals). The fourth electron forms a π-bond. The π-electrons are delocalised over the whole sheet, and as they are mobile, graphite conducts heat and electricity. Conductance can occur in a sheet (layer) but not from one sheet to another.

These layers are stacked on one another such that atoms of alternate layers lie vertically beneath one another. The interlayer distance, i.e. the distance between the layers is 340 pm. The interlayer distance is appreciably large, more than twice the covalent radius of carbon. This indicates that the layers are not joined together by covalent bonds but are joined together by weak van der Waals force. The layer therefore can slip over one another giving a lubricating property to graphite. The wide spacing between the layers means that the atoms do not pack together to fill space very effectively. Thus, the density of graphite (2.22 g cm^{-3}) is less than that of diamond (2.22 g cm^{-3}).

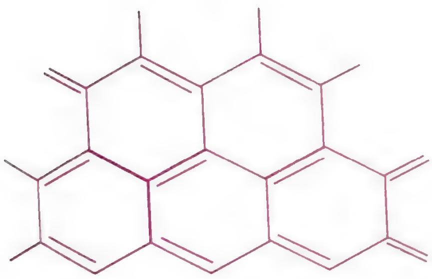
Graphite is of two forms: α and β.

In α-graphite, the layers are arranged in the sequence ABAB... with the third layer exactly above the first layer.

In β-graphite, the layers are arranged as ABC ABC ...... The two forms are interconvertible. Heating turns β into α and grinding turns α into β.



(a)



(b)

Fig. 7.7 Structure of graphite (a and b)

Properties:

1. Since each C-atom is sp^2 hybridised, C–C bond length in graphite is 141.5 pm.
2. Since the layers of C-atoms are held together by weak van der Waals forces of attraction, the layers can slip over one another. Thus, graphite is soft and acts as a good lubricating agent.
3. In each layer, each C-atom is sp^2 hybridised and is linked to three C-atoms by covalent bonds, one electron on each C-atom (in 2*p* orbital) is free and gets delocalised throughout the layer structure. Due to the presence of delocalised electron density throughout the layer structure, graphite acts as good conductor of heat and electricity.
4. The average value of (C–C) bond order in graphite is 1.33. Since each C-atom in graphite is sp^2 hybridised and is connected to three others by one double bond and two single bonds.

$$\therefore \text{Bond order} = \frac{\text{Double bond} + 2 \text{ single bond}}{\text{No. of atoms attached to other 3 C-atoms}}$$

$$= \frac{2+2}{3} = \frac{4}{3} = 1.33$$

5. Due to strong C–C covalent bonding within the sheets, much higher thermal energy is required to break the bonds. This is why its melting point is high (= 3700°C).
6. Graphite burns in air at 700–800°C to give CO_2.

$$\underset{\text{(Graphite)}}{C_{(s)}} + \underset{\text{(Air)}}{O_{2(g)}} \xrightarrow{700-800^\circ C} CO_{2(g)}$$

7. Graphite is chemically more active than diamond.
8. It is not attacked by alkalis and dilute acids.
9. When treated with conc HNO_3 or conc H_2SO_4, it is oxidised to insoluble yellowish green substance known as graphitic acid ($C_{11}H_4O_5$).
10. With alkaline $KMnO_4$, it is oxidised to mellitic acid $[C_6(COOH)_6]$ and oxalic acid.
11. With chromic acid ($HCrO_4$) it forms $CO_{2(g)}$.
12. Graphite is thermodynamically more stable than diamond and its free energy of formation ($\Delta^{\ominus}_f G$) is 1.9 kJ mol^{-1} less than diamond at room temperature and ordinary pressure.

    Thermodynamically it is favourable for diamond to convert into graphite. Normally they do not do so because there is a high energy of activation (E_{act}) for the process. If this energy is available, the change does occur and diamond tipped drills do burn out and form graphite if they get too hot. The reverse process is not thermodynamically possible, and it requires very forcing high energy conditions to convert graphite to diamond. Graphite can be converted to synthetic diamond at 1600°C by a pressure of 50,000–60,000 atmosphere (Graphite $\xrightarrow[50,000-60,000 \text{ atm.}]{1600^\circ C}$ Diamond).
13. When graphite is heated with vapours of K, Rb, Cs at 300°C it forms C_8 M. Graphite is diamagnetic but C_8 M is paramagnetic.

Uses:

1. It used as lubricant for the fast moving parts of the machinery. Since graphite is non-voatile in nature, it can be used as a lubricating agent for the machinery parts which operate at a very high temperature. It is a greasy substance.
2. Since graphite is soft and marks paper black, mixed with desired quantities of wax or clay, graphite is used for making cores of lead pencils. Graphite is also known as *black lead* or *plumbago*.
3. As graphite has a high melting point, it is used for making refractory crucibles, which are used for melting metals in industry.
4. It is used for lining and for making electrodes of electric furnaces.
5. It is used as a moderator, i.e. for reducing the speed of fast moving neutrons in an atomic reactor.
6. It is used as a reducing agent, in steel manufacture.

The difference between the properties of diamond and graphite is given in Table 7.6.

Table 7.6 Difference between diamond and graphite

Diamond	Graphite
1. Occurs in nature in the free state.	1. Occurs naturally and is also manufactured artifically.
2. Hardest natural substance.	2. Soft and greasy to touch.
3. Occurs as octahedral crystals.	3. Occurs as hexagonal crystal.
4. Insoluble in all solvents.	4. Soluble in some solvents.
5. Burns in air at 900°C to give CO_2.	5. Burns in air at 700–800°C to give CO_2.
6. It is transparent and has high refractive index (2.45).	6. It is black and opaque.
7. It is a bad conductor of electricity and good conductor of heat.	7. It is good conductor of electricity and good conductor of heat.

Oil dag

Colloidal graphite sol. in oil, whose composition is as follows:

Petroleum oil	85%
Graphite	10%
Binders	5%

The following is a list of functions of oil dag:

1. Protects against corrosion.
2. Lubricates effectively up to 900°F (482°C).
3. Reduces maintainance cost through more effective lubrication.
4. Reduces break in time for new equipments.
5. Solid lubricating film prevents metal to metal contact, thus greatly facilitating disassembly in many appliances.

Aquadag

'Aqueous deflocculated adheson graphite.' It is a colloidal suspension of fine particles of graphite in water and is used especially as a lubricant.

It forms a smooth continuous dry film with extra long wear life.

7.6.1.3 Fullerenes

Till 1985, only two crystalline allotropes of carbon were known, namely diamond and graphite. In 1985, the third crystalline allotrope of carbon, i.e. *Fullerene*, was discovered collectively by three scientists: R.E. Smalley and R.F. Curl of Rice University, Houston, Texas (USA) and H.W. Kroto of University of Sussex, Brighton (UK). For this discovery, these three scientists shared the Noble Prize in chemistry in 1996.

Preparation: Fullerenes constitute a new family of carbon allotropes consisting of large spheroidal molecules having composition, C_{2n}, where $n \geq 30$. Initially, these were prepared by evaporation of graphite using a laser. A more practical method involves the heating of graphite in an electric arc in the presence of an inert gas such as helium (He) or argon (Ar). The sooty material formed by condensation of vapourised C_n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of other fullerenes consisting of even number of carbon atoms up to 350 or above. C_{60} and C_{70} can be readily separated from the fullerene soot by the extraction of toluene followed by chromatographic separation over alumina (Al_2O_3). The complete process can be represented as follows:

$$\text{Graphite} \xrightarrow[\text{Inert gas (He or Ar)}]{\text{Electric arc}} \text{Vapourised carbon} \xrightarrow{\text{Condensation}} \underset{(C_{60} + \text{little } C_{70})}{\text{Fullerene soot}} \xrightarrow[(Al_2O_3)]{\text{Extraction + Chromatographic separation}} (C_{60} + C_{70})$$

Unlike graphite or diamond, fullerenes dissolve in organic solvents to give coloured solutions. A solution of C_{60} in toluene is purple, whereas that of C_{70} is orange red. In fact, fullerenes are the only pure form of carbon since they do not have dangling edge or surface bonds to be attracted to other atoms as in the case of diamond or graphite.

Structure: Fullerene C_{60}, as shown in Fig. 7.8, has been named Buckminsterfullerene in honour of American Architect, Robert Buckminster Fuller, the who designed geodesic dome structure having hexagonal and pentagonal patterns.

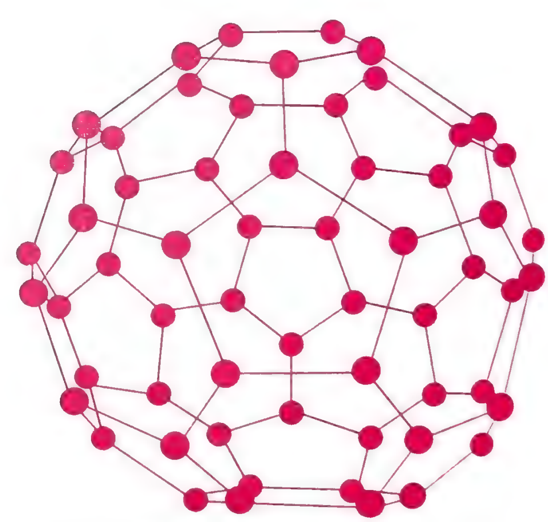


Fig. 7.8 Structure of Buckminsterfullerene (C_{60})

Note:

i. There are 12 five-membered rings.
ii. There are 20 six-membered rings.
iii. Six-membered rings are fused to other six-membered as well as five-membered rings.
iv. Five-membered rings are fused to only six-membered rings.
v. There are both single and double bonds.

The general name *fullerene* refers to the family of spheroidal carbon cage molecules. The shape of C_{60} resembles that of a soccer ball. It contains 12 five-membered ring and 20

six-membered rings. Six-membered rings are fused to other six-membered as well as five-membered rings. However, five-membered rings are fused to only six-membered rings. All the carbon atoms are equivalent and undergo sp^2 hybridisation. There are both single and double bonds, with C – C distances of 145.3 and 138.5 pm, respectively.

BUCKY BALLS AND BUCKY TUBES: THE FULLERENE SAGA

Laser evaporation of graphite did produce evidence for the formation of linear molecules with five to nine carbon atoms, which had been observed in interstellar space. In addition, several other carbon clusters containing 40 to 100 (always an even number) of carbon atoms were formed.

Subsequent research in various countries led to the discovery of other larger spheroidal carbon cage structure molecules and carbon nanotubes. The general name fullerenes is given to these new carbon species formed by the condensation of the carbon vapours. They are also known as *Bucky balls* and *Bucky tubes*.

Methode to produce fullerences: By passing an electric arc discharge through graphite rods in an atmosphere of helium to produce carbon soot and the extraction of the soot with an organic solvent such as benzene gave a soluble fraction, which contained mainly C_{60} and a small quantity of C_{70} with traces of higher fullerenes. Pure C_{60} and C_{70} can be isolated from this fraction by chromatography.

C_{60} molecule resembles a soccer ball and C_{70} resembles a rugby ball. **Some salient features of C_{70} are as follows:**

1. Twelve five-membered rings.
2. Twenty-five six-membered rings.
3. Six-membered rings are fused to both the other six-membered and five-membered rings.
4. Five-membered rings are fused with six-membered rings only.

Electric arc evaporation of graphite also produces carbon nanotubes which consist of cylindrical tubes formed by graphite layers which are capped by fullerene-like hemispheres. They are used in catalysis, nanotechnology and electronics.

Properties:

1. Carbon atom in fullerene is sp^2 hybridised.
2. The fullerenes being covalent are soluble in organic solvents.
3. Fullerenes can be reduced electrochemically and react with elements of group 1 to form solids such as K_3C_{60}. This compound behaves as a superconductor below 18 K, which implies that is carries electric current with zero resistance.
4. It reacts with O_SO_4 which adds one of the double bonds in the cage.
5. It also forms complexes with platinum.

Uses:

1. At present, fullerenes do not have any practical use. However, they find applications in nanotechnology.

Table 7.7 Comparison of crystalline allotropes of carbon

	Crystalline allotropes of carbon		
	Diamond	Graphite	Fullerene
Hybridisation of carbon	sp^3	sp^2	sp^2
Bond length (C–C) (pm)	154	141.5	145.3 and 138.3
$\Delta_f H^\ominus$ (kJ mol^{-1})	1.90	0	38.1

Some important points on the crystalline allotropes of carbon:

a. Graphite is thermodynamically the most stable allotrope of carbon. Its standard enthalpy of formation $\Delta_f H^\ominus$ is assigned a value of zero. The standard enthalpy of formation of diamond and C_{60} are 1.90 and 38.1 kJ mol^{-1}, respectively (Table 7.7).

b. Although the conversion of diamond into graphite is thermodynamically favourable, it normally does not occur because of high activation energy required for the process.

c. The conversion of graphite into diamond is thermodynamically not possible but can be done only under forced conditions. Graphite can be converted into diamond at 1873 *K* under a pressure of 50,000–60,000 atm.

$$\text{Graphite} \xrightarrow[\text{50,000 – 60,000 atm}]{\text{1873 K}} \text{Diamond}$$

d. Diamond has the highest thermal conductivity of any known substances (about five times that of Cu), although it is a bad conductor of electricity. It is due to its high thermal conductivity. This is why tools having diamond tip do not overheat and, hence, are extensively used for drilling and cutting purposes.

e. The value of diamond is expressed in terms of its cut, carat (weight) and clarity (purity). The weight of diamond is expressed in terms of *carats*. The famous *Kohinoor diamond*, which at present decorates the crown of England's queen, weighs 108.93 carat.

$$\boxed{1 \text{ carat} = 200 \text{ mg}}$$

However, when it was taken from India to England, it weighed 181 carat. To restore its brilliance and lusture 43% of its original weight was shed.

2. Amorphous allotropic form of carbon.

a. *Coke* **b.** *Charcoal* **c.** *Carbon black.*

These are all impure forms of graphite or fullerenes.

7.6.2 PROPERTIES OF CARBON

7.6.2.1 Atomic and Physical Properties

Carbon exists in crystalline as well as amorphous allotropic forms (for details, refer to Section 7.6.1). The X-ray studies have revealed that amorphous forms of carbon also have extremely fine crystals. Hence, these are also known as *microcrystalline carbons*.

Atomic and physical properties of carbon are given in Table 7.1, Section 7.3.

7.6.2.2 Chemical Properties

Of all the allotropic forms of carbon, charcoal due to its high surface area is the most reactive form of carbon. The other forms such as diamond, graphite, etc. are denser and hence less reactive.

1. **Combustion:** All the allotropic forms of carbon burn in air or oxygen forming CO_2 (in excess of O_2) and CO (in limited supply of O_2).

$$C + \underset{\text{Excess}}{O_2} \longrightarrow CO_2$$

$$2C + \underset{\text{Limited supply}}{O_2} \longrightarrow 2CO$$

This shows that all allotropes of carbon are identical.

2. **As reducing agent:** Carbon acts as strong reducing agent. It reduces many metallic oxides to corresponding metals, sulphate to sulphides, and water to hydrogen. These reactions occur at high temperatures.

$$PbO + C \longrightarrow Pb + CO$$

$$PbSO_4 + 4C \longrightarrow PbS + 4CO$$

$$\underset{\text{Steam}}{H_2O} + C \xrightarrow{\text{Red heat}} \underbrace{CO + H_2}_{\text{Water gas}}$$

3. **Reactivity towards acids:** Charcoal dissolves slowly in hot dil HNO_3 to form brown coloured substance known as *artificial tannin.*

Carbon is oxidised to CO_2 with conc HNO_3:

$$C + \underset{\text{Conc}}{4HNO_3} \longrightarrow CO_2 + 4NO_2 + 2H_2O$$

Hot and conc H_2SO_4 oxidises C to CO_2. A small quantity of mellitic acid (benzene hexacarboxylic acid) is also formed.

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$12C + 9H_2SO_4 \longrightarrow \underset{\text{Mellitic acid}}{C_6(COOH)_6} + 6H_2O + 9SO_2$$

4. **Combination with other elements:**

a. Carbon reacts with sulphur when the vapours of sulphur are passed over red hot carbon to form carbon disulphide, CS_2.

$$C + 2S \longrightarrow CS_2$$

b. When electric arc is stuck between carbon electrodes in the presence of hydrogen, acetylene is formed.

$$2C + H_2 \longrightarrow C_2H_2$$

c. On heating with carbon, Be forms beryllium carbide (Be_2C).

$$2Be + C \rightarrow Be_2C$$

d. On heating with carbon, certain oxides form carbides.

$$CaO + 3C \xrightarrow{2000°C} \underset{\text{Calcium carbide}}{CaC_2} + CO$$

$$2Al_2O_3 + 9C \xrightarrow{2000°C} \underset{\text{Aluminium carbide}}{Al_4C_3} + 6CO$$

$$SiO_2 + 3C \xrightarrow{2000°C} \underset{\text{Carborundum}}{SiC} + 2CO$$

7.6.3 Uses of Carbon

1. Graphite fibres reinforced plastics are prepared by embedding or reinforcing graphite fibres into a light weight matrix such as epoxy resin, polyester resin or polyamide. These are high strength, light weight composites. The composites are used in products such as tennis rackets, fishing rod, aircrafts and canoes.
2. Since graphite is a good conductor of electricity, it is used for making electrodes in batteries and industrial electrolysis.
3. Crucibles made up of graphite are inert to the action of dilute acids and alkalis.
4. Graphite is used as a lubricant in heavy industry.
5. Graphite is used as a moderator for gas cooled nuclear reactors, where it slows down fast moving neutrons.
6. Diamond is a precious stone and is used in jewellery. It is measured in carat (1 carat = 200 mg). Diamond is also used for making drills or as an abrasive for cutting and polishing.
7. Activated charcoal, being highly porous, is used for absorbing poisonous gases in gas masks, in water filters to remove organic contaminators and in air-conditioning system to control odour. It is used to purify and decolourise sugar and as a catalyst for some reactions.
8. Carbon black is used as a black pigment in black ink and as filler in automobile tyres.
9. Coke is extensively used as a reducing agent in metallurgy and also as a fuel.

7.7 SILICON

Silicon is obtained by the reduction of silica. Silicon exists in two allotropic modifications: (i) Amorphous and (ii) Crystalline.

7.7.1 Amorphous Silicon

It is obtained by heating dry powdered silica with magnesium.

$$SiO_2 + 2Mg \longrightarrow Si + 2MgO$$

Properties:

1. Amorphous silicon is chemically more reactive than crystalline silicon.
2. It is brownish powder.
3. It burns brilliantly in oxygen.

$$Si + O_2 \longrightarrow SiO_2$$

4. It decomposes steam at red heat with the evolution of H_2.

$$Si + 2H_2O \longrightarrow SiO_2 + 2H_2\uparrow$$

5. Reaction with acids: It dissolves in the mixture of HNO_3 and HCl.
6. Reaction with bases: It dissolves readily in alkalis.

$$Si + 2KOH + H_2O \longrightarrow \underset{\text{Potassium silicate}}{K_2SiO_3} + 2H_2$$

$$Si + Na_2CO_3 \longrightarrow \underset{\text{Sodium silicate}}{Na_2SiO_3} + C$$

7. Reaction with metals: It combines with certain metals to form silicides.

$$2Mg + Si \longrightarrow \underset{\text{Magnesium silicide}}{Mg_2Si}$$

8. Reaction with non-metals: It ignites spontaneously in fluorine

$$Si + 2F_2 \longrightarrow SiF_4$$

Uses:

1. These alloys possess high strength, hardness and are resistant to the attack of acids.
2. In a high purity state, Si acts as semiconductor, i.e. it does not conduct electricity until certain electric voltage is applied but beyond that it conducts moderately. It is an insulator when pure; but when doped (doping is replacing Si atom by some other atom in pure silicon) with group 15 or group 13 elements, it becomes *p*-type (excess of electrons) or *n*-type (deficiency of electrons) semiconductor, respectively. These are used as transistors and semiconductor devices.
3. Very pure Si is also used to make computer chips.

7.7.2 Crystalline Silicon

It is obtained by the following methods:

1. By heating finely powdered sand or quartz with carbon in an electric furnace. A small amount of iron is added to prevent the formation of carborundum, SiC.

   $$SiO_2 + 2C \longrightarrow Si + 2CO$$

2. On strongly heating amorphous silicon, it fuses; on cooling, it solidifies to give the crystalline form.

Properties:

1. It is very hard.
2. It does not burn in oxygen but readily combines with fluorine.
3. It dissolves in a mixture of HNO_3 and HF.
4. When fused with alkali, silicates are formed.

   $$Si + Na_2CO_3 \longrightarrow Na_2SiO_3 + C$$

   High purity Si : It can be prepared by reducing $SiCl_4$ with Mg.

   $$SiCl_4 + 2Mg \longrightarrow Si + 2MgCl_2$$

   $MgCl_2$, being water soluble, is washed away and the final purification of silicon takes place by zone-refining.

Uses: In the manufacture of alloys:

Alloy	Composition		Uses
Silicon bronze	Zn 1.0% Sn 1.0% Mn 1.5% Fe 0.50%	Si 2.8-4.01% Al 0.01% Pb 0.02% Cu 90%	Used to coat the surfaces subject to corrosion
Manganese silicon bronze	Cu 60.5% Pb 1.7% Mn 2.75%	Si 1% Zn 34.05%	For making hydraulic piston shoes, cylinder liners, etc.

7.8 GERMANIUM

1. Germanium is silvery white, hard and brittle.
2. It has no allotrope.
3. It is more reactive than silicon.
4. Like Si, it is used as a semiconductor, especially in the fabrication of transistors.
5. Germanium is not attacked by dil HCl; however, on heating Ge in a stream of HCl gas, germanium chloroform ($GeHCl_3$) is formed.

   $$Ge + 3HCl \xrightarrow{\Delta} \underset{\text{Germanium chloroform}}{GeHCl_3} + H_2\uparrow$$

7.9 TIN

1. Tin does not occur free in nature.
2. The most important ore of tin is cassiterite, SnO_2, which is also known as *tinstone*. It is usually associated with tungstates of iron ($FeWO_4$) and manganese ($MnWO_4$).
3. Tin is silvery white metal; m.pt. 232°C, b.pt. 2270°C.
4. Tin is not affected by air.
5. It is malleable and ductile; however, at 200°C, it becomes brittle and can be powdered.
6. Tin produces a crackling sound on bending, which is known as cry tin or tin cry. This is due to rubbing of metal crystal over one another.
7. Allotropic modifications of tin: Grey, white and rhombic.

   $$\text{Grey} \xrightleftharpoons{18°C} \text{White} \xrightleftharpoons{170°C} \text{Rhombic}$$

   Density ($g\ cm^{-3}$) 5.74 7.32 6.55

   a. The three forms are interconvertible. White tin is not only the heaviest but also the most stable form.

   b. Conversion of white tin into grey tin in cold countries is accompanied by decrease in density, i.e. increase in volume.

   c. Grey tin is very brittle and easily decomposes into powdered form. This is termed as *tin disease or tin pest or tin plague*.

   d. As compared to group 1, 2 and 13 metals, tin is much less reactive.

   e. On heating at 1500–1600°C in the presence of oxygen, it burns with bright flame forming stannic oxide, SnO_2.

   $$Sn + O_2 \xrightarrow{1500-1600°C} SnO_2$$

   f. It is not affected by water.

   g. Molten tin decomposes steam, thus liberating hydrogen.
8. Tin is not attacked by organic acids. This property is utilised for tinning cooking utensils made of copper or brass. Organic acids present in food attack the utensils which are made of copper, brass etc. This may cause food poisoning. The vessels are protected by tinning, i.e. depositing a thin layer of tin on the surface of the utensils. The vessel to be tinned is perfectly cleaned and a pinch of NH_4Cl is sprinkled to remove the oxide film. A little tin is fused on the clean surface and it is then rubbed over with the help of a cotton rag to have a uniform layer.

Tin is also used in forming a protective coating over iron. The process of depositing tin over iron sheets or steel is called *tin plating*. Tin plating is done either mechanically or electrically.

9. Reactions with acids:

a. With HCl: Tin dissolves slowly in dil HCl but readily in conc HCl.

$$Sn + 2HCl \longrightarrow SnCl_2 + H_2\uparrow$$

b. With H_2SO_4: Tin dissolves in conc H_2SO_4 as well as in dil H_2SO_4.

$$\overset{(0)}{Sn} + \underset{\text{dil}}{H_2SO_4} \longrightarrow \overset{(+2)}{SnSO_4} + H_2\uparrow$$

$$\overset{(0)}{Sn} + \underset{\text{conc}}{4H_2SO_4} \longrightarrow \overset{(+4)}{Sn(SO_4)_2} + 2SO_2\uparrow + 4H_2O$$

c. With HNO_3: Tin dissolve in dil HNO_3 due to the formation of soluble tin(II) nitrate or stannous nitrate.

$$4Sn + 10HNO_3 \longrightarrow \underset{\text{Stannous nitrate}}{4\,Sn(NO_3)_2} + \underset{\text{Ammonium nitrate}}{NH_4NO_3} + 3H_2O$$

Tin is oxidised to metastannic acid by conc HNO_3

$$Sn + 4HNO_3 \longrightarrow \underset{\text{Metastannic acid}}{H_2SnO_3} + \underset{\text{Nitrogen dioxide}}{4NO_2\uparrow} + H_2O$$

d. Organic acids have no action.

10. Reaction with alkali: Tin dissolves in hot alkali solutions to form stannates.

$$Sn + 2NaOH + H_2O \longrightarrow \underset{\text{Sodium stannate}}{Na_2SnO_3} + 2H_2\uparrow$$

Uses:

1. For tinning utensils made up of brass, copper etc.
2. For tin plating.
3. Tin amalgam is used for making mirrors.
4. For making useful alloys (Table 7.8).

Table 7.8 Some useful alloys of tin

Alloy	Composition	Uses
Bell metal	80% Cu, 20% Sn	Bell and gongs
Type metal	3% Sn, 82% Pb, 15% Sb	Printing types
Britannia metal	86% Sn, 12% Sb, 2% Cu	Cheap table ware
Solder	67% Sn, 33% Pb	For soldering
Rose metal	28% Sn, 22% Pb, 50% Bi	For electric fuses
Bronze	75-90% Cu, 10-25% Sn,	For making utensils, statues and coils
Pewter	75% Sn, 25% Pb	For making cups, mugs and other utensils
White metal	82% Sn, 12% Sb, 6% Cu	For making tableware

7.10 LEAD

1. Lead is mainly found in the form of sulphide. The ore is known as galena, PbS (lead content varies from 6 to 8%). It is usually associated with zinc blende, iron pyrites and traces of silver (~ 0.1%). The other less important ores of lead are:

Anglesite	$PbSO_3$
Cerussite	$PbCO_3$
Lanarkite	$PbO{\cdot}PbSO_4$

2. It is a bluish-grey metal and has bright metallic lustre when freshly cut. However, on exposure to air, it becomes dull due to formation of a thin layer of oxide on the surface.
3. It is soft in nature and that is why can be cut with knife and scratched with a finger nail.
4. It is malleable, but not very ductile.
5. It leaves black mark on paper.
6. It is a poor conductor of electricity.
7. It is a heavy metal with specific gravity 11.35.
8. Reactivity with air:

a. It is not affected by dry air; but with most air, a thin film of basic carbonate is formed on its surface, which prevents further reaction.

b. When heated with air or oxygen, it forms litharge (or lead monoxide) which changes to red lead (or Pb_3O_4).

$$2\,Pb + O_2 \xrightarrow{\Delta} 2PbO$$

$$3Pb + 2O_2 \xrightarrow{\text{High temp.}} Pb_3O_4$$

9. Reactivity with water: It is not affected by pure air-free water, except at the boiling point. It dissolves slowly in water containing dissolved oxygen.

$$2Pb + 2H_2O + O_2 \longrightarrow 2Pb(OH)_2$$

The dissolution of lead in water is known as *plumbosolvency*. If the water contains nitrates, ammonium salts and organic acids, plumbosolvency increases. The presence of soluble sulphates, phosphates, carbonates etc. decreases plumbosolvency due to formation of a protective thin layer of insoluble lead salts.

$$Pb^{2+} + SO_4^{2-} \longrightarrow \underset{\text{Lead sulphate}}{PbSO_4\downarrow}$$

$$Pb^{2+} + PO_4^{3} \longrightarrow \underset{\text{Lead phosphate}}{Pb_3(PO_4)_2\downarrow}$$

$$Pb^{2+} + CO_3^{2-} \longrightarrow \underset{\text{Lead carbonate.}}{PbCO_3\downarrow}$$

Lead pipes are often used to transport drinking water. In order to minimise plumbosolvency, i.e. dissolution of lead

in water, hard water is first passed through the lead pipes in order to deposit the protective layer on the inner surface of the pipes.

10. Reactivity with acids: Dilute HCl only slightly attacks lead as a thin film of $PbCl_2$ is formed on the surface, which prevents further action, whereas powdered lead readily dissolves in conc HCl with the evolution of hydrogen.

$$\underset{\text{Conc}}{Pb + 2HCl} \longrightarrow PbCl_2 + H_2\uparrow$$

$$\underset{\text{Excess (conc)}}{PbCl_2 + 2HCl} \longrightarrow \underset{\text{Chloroplumbous acid}}{H_2PbCl_4}$$

Dilute H_2SO_4 does not attack lead readily, but hot conc H_2SO_4 dissolves lead with the evolution of SO_2. However, the reaction becomes slow due to formation of insoluble layer of $PbSO_4$ on the surface.

$$Pb + 2H_2SO_4 \xrightarrow{230°C} \underset{\text{White ppt}}{PbSO_4\downarrow} + SO_2 + 2H_2O$$

HNO_3: Lead reacts with both dil HNO_3 and conc HNO_3. HNO_3 is the best solvent for Pb. With dil HNO_3, nitric oxide (NO) (g) is produced, whereas with conc HNO_3, NO_2 is produced.

$$[Pb + \underset{\text{dil}}{2HNO_3} \longrightarrow 2Pb(NO_3)_2 + 2H] \times 3 \quad ...(7.1)$$

$$[HNO_3 + 3H \longrightarrow NO + 2H_2O] \times 2$$

$$\boxed{Pb + \underset{\text{Dil}}{8HNO_3} \longrightarrow \underset{\text{Lead nitrate}}{3Pb(NO_3)_2} + \underset{\text{Nitric oxide}}{2NO} + 4H_2O}$$

$$Pb + \underset{\text{Conc}}{2HNO_3} \longrightarrow Pb(NO_3)_2 + 2H \quad ...(7.2)$$

$$[HNO_3 + H \longrightarrow NO_2 + H_2O] \times 2$$

$$\boxed{Pb + \underset{\text{Conc}}{4HNO_3} \longrightarrow \underset{\text{Lead nitrate}}{Pb(NO_3)_2} + \underset{\text{Nitrogen dioxide}}{2NO_2} + 2H_2O}$$

Ionic equation for above reactions (7.1) is as follows:

$$[Pb \longrightarrow Pb^{2+} + 2e^-] \times 3 \quad ...(7.3)$$

$$[4H^{\oplus} + 3e^- + \underset{\text{Dil}}{NO_3^{\ominus}} \longrightarrow NO + 2H_2O] \times 2 \quad ...(7.4)$$

$$3Pb + 8H^{\oplus} + 2NO_3^{\ominus} \longrightarrow 3Pb^{2+} + 2NO + 4H_2O \quad ...(7.5)$$

Adding 6 $NO_3^{\ominus}$ on both sides of Eq. (7.5), we have

or

$$3Pb + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

Ionic equation for reaction (7.2) is as follows:

$$Pb \longrightarrow Pb^{2+} + 2e^- \quad ...(7.6)$$

$$\left[2H^{\oplus} + e^- + \underset{\text{Conc}}{NO_3^{\ominus}} \longrightarrow NO_2 + H_2O\right] \times 2 \quad ...(7.7)$$

$$\boxed{Pb + 4H^{\oplus} + 2NO_3^{\ominus} \longrightarrow Pb^{2+} + 2NO_2 + 2H_2O} \quad ...(7.8)$$

Adding $2NO_3^{\ominus}$ on both sides of Eq. (7.8), we get

$$Pb + 4HNO_3 \longrightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$$

Organic acids: Organic acids dissolves lead in the presence of oxygen. Pb is corroded by CH_3COOH

$$2Pb + \underset{\text{Acetic acid}}{4CH_3COOH} + O_2 \longrightarrow \underset{\text{Lead acetate}}{2Pb(CH_3COO)_2} + 2H_2O$$

11. Reactivity with base: Lead dissolves in NaOH with the evolution of hydrogen.

$$Pb + 2NaOH \longrightarrow \underset{\text{Sodium plumbite}}{Na_2PbO_2} + H_2\uparrow$$

12. Reactivity with non-metals:

$$Pb + S \longrightarrow \underset{\text{Lead sulphide}}{PbS}$$

$$Pb + 2Cl_2 \longrightarrow \underset{\text{Lead tetrachloride}}{PbCl_4}$$

Uses:

1. To make alloys such as solder, type metal etc.
2. For making pipes, which are used to carry water.
3. For making chambers, used in the manufacture of H_2SO_4.
4. In the preparation of lead pigments.
5. For making telegraph and telephone wires which are to buried in earth.
6. In fine arts, on account of the ease with which it can be worked out, cut and soldered and due to its resistance to water and many acids.

7.11 COMPARISON OF CARBON AND SILICON WITH OTHER GROUP 14 ELEMENTS

Carbon and silicon differ from the other group 14 elements, i.e. germanium, tin and lead, in the following ways:

1. **Electronic configuration:** Both carbon and silicon have noble gas core beneath the valence shell electrons, whereas Ge, Sn and Pb have intervening fully filled *d* and/or *f* shell between the valence shell electrons and the noble gas core.
2. **Metallic character:** Both C and Si are non-metals due to high sum of the first four ionisation enthalpies, whereas Ge is a metalloid, and Sn and Pb are metals.
3. **Valency:** C and Si show tetravalency and do not give tetravalent (M^{4+}) or bivalent (M^{2+}) ions. However, Ge, Sn and Pb show tetravalency as well as form bivalent metal ions, i.e. Ge^{2+}, Sn^{2+} and Pb^{2+}.
4. **Oxidation states:** Both C and Si exhibit oxidation state of +4 only, whereas Ge, Sn and Pb show both +4 and +2 oxidation states due to inert pair effect.
5. **Catenation:** Carbon, and to some extent silicon, have a tendency for catenation, whereas others do not show this property to great extent.
6. **Nature of dioxides:** CO_2 and SiO_2 are acidic, whereas GeO_2 and SnO_2 are amphoteric; but PbO_2 is weakly basic.
7. **Formation of acids:** Carbon and silicon form acids of type HOOC–COOH (oxalic acid) and HOOSi–SiOOH (silicon oxalic acid), while others do not.

7.12 COMPARISON OF CARBON AND SILICON

The first two elements of group 14, carbon and silicon, have many similarities in their properties as they have the same number of valence shells electrons, i.e. 4. However, they show many dissimilarities too due to difference in the number of electrons in the penultimate shell.

7.12.1 Similarities Between Carbon and Silicon

1. **Electronic configuration:** Both carbon and silicon have four electrons in their valence shell.

   C (Z = 6): 2, 4 ($1s^2 2s^2 2p^2$) Si (Z = 14): 2, 8, 4 ($1s^2\ 2s^2 2p^6 3s^2 3p^2$)

2. **Occurrence:** Both C and Si are widely distributed in nature. Carbon is an essential constituent of vegetable and animal kingdom, i.e. organic compounds, while silicon is an essential constituent of mineral kingdom, i.e. inorganic compounds.
3. **Valency:** Both are tetravalent and show a covalency of four and form compounds by sharing of electrons.
4. **Allotropy:** Both exist in more than one form, i.e. exhibit allotropy.
5. **Catenation:** Both possess the property of catenation.
6. **Non-metal:** Both are typically non-metallic in nature.
7. **Formation of hydrides:** Both form a number of covalent hydrides.

   CH_4 C_2H_6 C_3H_8 C_4H_{10}

   SiH_4 Si_2H_6 Si_3H_8 Si_4H_{10}

   These are all colourless gases and burn in oxygen to form oxides.

   $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

   $SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$

   Both can be prepared by similar methods, i.e. by the action of water or acids on carbides and silicides, respectively.

   $Be_2C + 4HCl \longrightarrow 2BeCl_2 + CH_4$

   $Mg_2Si + 4HCl \longrightarrow 2MgCl_2 + SiH_4$

8. **Formation of oxides:** Both burn in oxygen to produce acidic oxides.

   $C + O_2 \longrightarrow CO_2$

   $Si + O_2 \longrightarrow SiO_2$

9. **Formation of halides :** Both form covalent halides.

   CF_4 CCl_4 CBr_4 $CHCl_3$

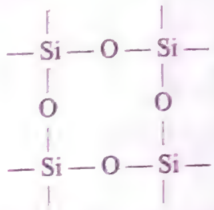
   SiF_4 $SiCl_4$ $SiBr_4$ $SiHCl_3$

10. **Formation of acids:** Both form similar type of acids.

    H_2CO_3 Carbonic acid — H_2SiO_3 Silicic acid

    COOH–COOH Oxalic acid — SiOOH–SiOOH Silicon oxalic acid

7.12.2 Dissimilarities Between Carbon and Silicon

Carbon	Silicon
1. Carbon has two electrons in the penultimate shell (2, 4).	1. Silicon has eight electrons in the penultimate shell (2, 8, 4).
2. It is black solid with m.pt. 3500°C.	2. It is reddish-brown solid with m.pt. 1410°C.
3. It is a bad conductor of electricity, except graphite which conducts electricity.	3. It is a bad conductor of heat and electricity.
4. Carbon does not react with alkalis.	4. Silicon reacts with alkalis thus liberating H_2. $Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$
5. CO_2 is a gas having linear structure: O = C = O.	5. SiO_2 is a high melting point solid. 
6. The lower oxide (CO) is stable and neutral in nature.	6. The lower oxide (SiO) is unstable.
7. Carbon forms a large number of hydrides known as hydrocarbons. These are stable and not hydrolysed by water.	7. Silicon forms lesser number of hydrides which act as reducing agents. These are hydrolysed with the evolution of H_2.
8. It does not react with Cl_2 or Br_2 directly.	8. It reacts with Cl_2 and Br_2 at 500°C. $Si + 2Cl_2 \longrightarrow SiCl_4$
9. CCl_4 is a stable compound and does not get hydrolysed by water.	9. $SiCl_4$ easily gets hydrolysed.
10. The oxyacid, H_2CO_3, is unstable. It is best known in the form of salts, e.g., carbonates.	10. The oxyacid, H_2SiO_3, is stable. It is also known in the form of salts, e.g. silicates.
11. It does not form complexes due to inability to exceed its coordination number beyond 4. This is because it does not have *d*-orbitals in its valence shell.	11. It forms a number of complexes as silicon has vacant *d*-orbitals in its valence shell and thus can exceed its coordination number beyond 4 (i.e. 6).

7.13 COMPARISON BETWEEN SILICON AND TIN

7.13.1 SIMILARITIES BETWEEN Si AND Sn

1. **Allotropy:** Both show allotropy.
2. **Oxides:** Both form oxides (SiO_2 and SnO_2) which are acidic in nature.
3. **Hydrides:** Both form gaseous hydrides. Hydride of Si, SiH_4, is more stable. Tin gives a hydride, SnH_4, by the action of HCl on an alloy of tin and magnesium.
4. **Halides:** Both form similar halides. The fluorides SiF_4 and SnF_4 are known to form same silicofluorides, K_2SiF_6 and stannifluorides, K_2SnF_6. Their chlorides are colourless, volatile liquids which are easily hydrolysed.
5. **Reaction with alkalis:** Both dissolve in hot alkali solution with the evolution of H_2.

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$

$$Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2$$

7.13.2 DISSIMILARITIES BETWEEN Si AND Sn

1. **Metallic character:** Si is non-metal, whereas Sn is metalloid.
2. **Melting point:** Tin melts at 232°C, whereas melting point of Si is very high.
3. **Reaction with dilute acids:** Si does not react with dilute acids, whereas Sn reacts with dilute acids with the evolution of hydrogen, H_2.
4. **Salts:** Nitrates, sulphates and other salts of tin are known, but such compounds are rare in the case of Si.

7.14 COMPARISON OF TIN WITH LEAD

Similarities:

1. Both form highly unstable hydrides.
2. Both form halides, which are quite stable. The formation of such halides indicates that these elements have feeble electronegative character.
3. Although both tin and lead have electropositive character, being in the middle of the periodic table, they show feeble electronegative character in some of its compounds such as halides, metastannates, metaplumbates etc.
4. Both Sn and Pb form similar complexes, namely stannates and plumbates, respectively.
5. Action of caustic alkali: When caustic alkali, NaOH, is added to Sn(II) salt solution in the absence of air, $Sn(OH)_2$ is first precipitated which dissolves in excess of alkali to form stannite, SnO_2^{2-}.

$$Sn^{2+} + 2NaOH \xrightarrow[\text{of air}]{\text{Absence}} Sn(OH)_2\downarrow + 2Na^{\oplus}$$

$$Sn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sodium stannite}}{Na_2SnO_2} + 2H_2O$$

Similarity, Pb (II) also forms soluble sodium plumbite on reacting with excess of NaOH.

$$Pb^{2+} + 2NaOH \longrightarrow Pb(OH)_2\downarrow + 2Na^{\oplus}$$

$$Pb(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sodium plumbite}}{Na_2PbO_2} + 2H_2O$$

ILLUSTRATION 7.1

a. Select the member(s) of group 14 that (i) forms the most acidic dioxide, (ii) is commonly found in +2 oxidation state and (iii) used as semiconductor.

b. $[SiF_6]^{2-}$ is known, whereas $[SiCl_6]^{2-}$ not. Give possible reasons.

c. Diamond is covalent, yet it has high melting point. Why?

Sol.

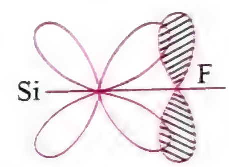
a. i. Carbon ii. Lead

iii. Silicon and germanium.

b. $[SiF_6]^{2-}$ is known, whereas $[SiCl_6]^{2-}$ is not. This is because

i. F is smaller in size as compared to Cl; so six flourine atoms can be easily accommodated around Si atom, but six large size Cl atoms cannot be accommodated around Si due to steric hinderance.

ii. The interaction between an electron pair present in 2*p*-orbital on F and vacant 3*d* orbital is stronger, resulting in $p\pi$–$d\pi$ bond formation, which is not so effective between large 3*p* orbital of Cl and 3*d* orbital of Si.



$p\pi$–$d\pi$ bond between Si and F

c. Diamond has a three-dimensional network involving strong C–C bonds, which are very difficult to break, and thus diamond has high melting point.

ILLUSTRATION 7.2

Give reason for the following:

a. The first ionisation enthalpy of carbon is greater than that of boron, whereas the reverse is true for the second ionisation enthalpy.

b. Solid carbon dioxide is known as dry ice.

c. Why does not silicon form an analogue of graphite?

Sol.

a. Electronic configuration of carbon is $1s^2\, 2s^2\, 2p^2$, whereas that of boron is $1s^2\, 2s^2\, 2p^1$. The first ionisation enthalpy of carbon is greater than that of boron due to its smaller size and higher effective nuclear charge. The valence shell electrons are more tightly bound to the nucleus; hence, for its removal greater amount of energy is required.

Hence, IE_1 of carbon > IE_1 of boron.

The second ionisation enthalpy of carbon is less than that of boron, as the removal of second electron in carbon has to be done from $2p$ orbital, whereas in boron, it has to be done from $2s$ orbital. First, $2s$ orbital is more penetrating as compared to $2p$ orbital; therefore, the electrons are more tightly bound. Also $2s^2$ configuration in C being fully filled is more stable than $2p^1$ in B. Because of these two reasons, IE_2 of C < IE_2 of B.

Alternate explanation:

1. C (Z = 6)

$$(2s^2 2p^2) \xrightarrow[\text{More energy is required due to high nuclear charge and small size}]{IE_1} 2s^2 2p^1 \xrightarrow[\text{Less energy is required, since } e^- \text{ has to be removed from less penetrated } p\text{-orbital}]{IE_2} \underset{\text{More stable configuration}}{2s^2 2p^0}$$

2. B(Z = 5)

$$(2s^2 2p^1) \xrightarrow[\text{Less energy is required due to less nuclear charge}]{IE_1} \underset{\text{More stable configuration}}{2s^2 2p^0} \xrightarrow[\text{More energy is required, since } e^- \text{ be removed from more penetrated } s\text{-orbital}]{IE_2} \underset{\text{Less stable configuration}}{2s^1}$$

Therefore, IE_1 of C > IE_1 of B and IE_2 of C < IE_2 of B.

b. Solid carbon dioxide on evaporation, change directly to the gaseous state without changing to the liquid state. It produces cooling during evaporation and does not wet the surface; therefore, solid CO_2 is known as dry ice.

c. Due to small size and high electronegativity of C, it is capable of forming $p\pi$–$p\pi$ bond, which occurs in graphite, whereas in Si, the size of the orbital involved, i.e., $3p$ in $p\pi$–$p\pi$ bond formation is large and hence multiple bond formation is not feasible in Si. Hence, silicon does not form an analogous of graphite.

ILLUSTRATION 7.3

Give the products formed on hydrolysis of (a) Al_4C_3 and (b) CaNCN.

Sol.

a. $$Al_4C_3 + 12H_2O \longrightarrow \underset{\text{Aluminium hydroxide (white ppt.)}}{4Al(OH)_3\downarrow} + \underset{\text{Methane}}{3CH_4\uparrow}$$

Aluminium carbide, Al_4C_3 on hydrolysis give a white precipitate of $Al(OH)_3$ alongwith methane (CH_4) gas.

b. $$CaNCN + 3H_2O \longrightarrow \underset{\text{Calcium carbonate (white ppt.)}}{CaCO_3\downarrow} + \underset{\text{Ammonia}}{2NH_3\uparrow}$$

Calcium cyanamide (CaNCN) on hydrolysis gives a white precipitate of calcium carbonate ($CaCO_3$) alongwith ammonia (NH_3) gas.

ILLUSTRATION 7.4

Identify (X) and (Y) in the following reactions.

$$PbS \xrightarrow[\text{in air}]{\text{Heat}} (X)$$

$$(X) + PbS \xrightarrow{(Y)} Pb + SO_2$$

Sol. PbS on heating in air produces either PbO or $PbSO_4$; hence, (X) is PbO or $PbSO_4$.

$$\underset{(X)}{2PbO} + PbS \xrightarrow{(Y)=?} 3Pb + SO_2$$

$$\text{or } \underset{(X)}{PbSO_4} + PbS \xrightarrow{(Y)=?} 2Pb + 2SO_2$$

(Y) is heat at high temperature, in the absence of air.

ILLUSTRATION 7.5

Arrange the following in increasing order:

a. First ionisation enthalpy: Mg, Al, Si, Na

b. Extent of hydrolysis: CCl_4, $MgCl_2$, $AlCl_3$, $SiCl_4$

c. Reducing power: $GeCl_2$, $SnCl_2$, $PbCl_2$

d. Oxidising power: $GeCl_4$, $SnCl_4$, $PbCl_4$

e. pH of the solution: NaCl, $BeCl_2$, $MgCl_2$, $AlCl_3$

Sol.

a. Increasing order of the first ionisation enthalpy:

Na < Al < Mg < Si

The valence electronic configuration of these elements are as follows:

Na (Z = 11)	$3s^1$
Mg (Z = 12)	$3s^2$
Al (Z = 13)	$3p^1$
Si (Z = 14)	$3p^2$

These elements belong to the same period. Along the period (→), effective nuclear charge increases. Hence, IE_1 should increase as Na < Mg < Al < Si. But Al has lower IE_1 value as compared to Mg due to penetration effect. Hence, the order reverses at Al and becomes:

Na < Al < Mg < Si

b. Increasing extent of hydrolysis:

$CCl_4 < MgCl_2 < AlCl_3 < SiCl_4$

In covalent halides, hydrolysis occurs as a result of coordination of a water molecule to the less electronegative element. CCl_4 does not undergo hydrolysis due to the absence of d-orbitals in its valence shell. So it cannot expand its coordination number beyond 4. Thus, it cannot coordinate with water molecules.

c. Increasing reducing power:

$PbCl_2 < SnCl_2 < GeCl_2$

Among group 14 elements, the stability of lower oxidation states, i.e +2, increases down the group (↓) due to increase in inert pair effect.

d. Increasing oxidising power:

$GeCl_4 < SnCl_4 < PbCl_4$

Among group 14 elements, the stability of higher or group oxidation state, +4, decreases down the group (↓) due to increase in inert pair effect.

e. Increasing pH of the solution

$AlCl_3 < BeCl_2 < MgCl_2 < NaCl$

With increase in charge/radius ratio of the central ion, the tendency to polarise electron cloud in H_2O molecule and, hence, dissociation of O – H bond in H_2O molecule increases, i.e. more and more proton will be liberated and solution becomes more acidic and pH decreases. In the compounds mentioned, charge/radius ratio is in the order: $Na^{\oplus} < Mg^{2+} < Be^{2+} < Al^{3+}$ and hence extent of hydrolysis follows the order: $NaCl < MgCl_2 < BeCl_2 < AlCl_3$. This is why NaCl will be least acidic and $AlCl_3$ will be more acidic. In other words, pH of NaCl will be least and that of $AlCl_3$ will be maximum; hence the order: $AlCl_3 < BeCl_2 < MgCl_2 < NaCl$.

7.15 SOME IMPORTANT COMPOUNDS OF GROUP 14 ELEMENTS

7.15.1 Oxides of Carbon

Carbon forms many oxides as compared to other elements. These oxides differ from the other elements because they contain $p\pi$–$p\pi$ multiple bonds between C and O. Two of these oxides namely CO and CO_2, are extremely stable and most important. Three less stable oxides are C_3O_2, C_5O_2 and $C_{12}O_9$. Others oxides that are even less stable are graphite oxide, C_2O and C_2O_3 etc.

7.15.1.1 Carbon Monoxide (CO)

Preparation:

1. By incomplete combustion of carbon and carbon containing fuels or direct oxidation of carbon in limited supply of air or oxygen.

$$2C + O_2 \longrightarrow 2CO$$

2. By heating oxides of heavy metals, e.g. iron, zinc etc. with carbon.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

$$ZnO + C \longrightarrow Zn + CO$$

3. In laboratory, pure CO is prepared by dehydration of formic acid (HCOOH) with conc H_2SO_4 at 373 K.

$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow[373\text{ K}]{H_2SO_4} \underset{\substack{\text{Carbon}\\ \text{monoxide}}}{CO} + H_2O$$

(H_2SO_4 acts as a dehydrating agent)

4. In laboratory, CO can be prepared by heating potassium ferrocyanide, $K_4[Fe(CN)_6]$, with conc H_2SO_4.

$$K_4[Fe(CN)_6] + 3H_2SO_4 \longrightarrow 2K_2SO_4 + FeSO_4 + \cancel{6HCN}$$

$$[\cancel{HCN} + 2H_2O \longrightarrow \cancel{HCOOH} + \cancel{NH_3}] \times 6$$

$$[\cancel{HCOOH} \longrightarrow H_2O + CO] \times 6$$

$$[\cancel{2NH_3} + H_2SO_4 \longrightarrow (NH_4)_2SO_4] \times 3$$

$$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO]$$

5. Commercially, CO is produced:

a. By passing steam over red hot coke.

$$C_{(s)} + H_2O_{(g)} \xrightarrow{473\text{–}1273\text{ K}} \underbrace{CO_{(g)} + H_{2(g)}}_{\text{Water gas}}$$

The mixture of CO and H_2 is known as **water gas** or **synthesis gas.**

b. When air is used instead of steam, a mixture of CO and N_2 is produced, which is called **producer gas.**

$$2C_{(s)} + O_{2(g)} + 4N_{2(g)} \xrightarrow{1273\text{ K}} \underbrace{2CO_{(g)} + 4N_{2(g)}}_{\text{Producer gas}}$$

Water gas and producer gas are very important industrial fuels. CO present in water gas or producer gas can undergo further combustion to form CO_2 with the liberation of heat.

Structure: The electron dot structure of CO may be represented as follows :

$\ddot{C}::\ddot{O}:$ or $\ddot{C}=\ddot{O}:$

In the above structures, C has six electrons while O has eight electrons in the valence shell. In order to complete the octet around C, O donates a pair of electrons.

$\boxed{:\overset{\ominus}{C}:::\overset{\oplus}{O}: \text{ or } :\overset{\ominus}{C}\equiv\overset{\oplus}{O}: \text{ or } :\overset{\ominus}{C}\equiv\overset{\ominus}{O}}$

CO is best represented as a resonance hybrid of the following two structures:

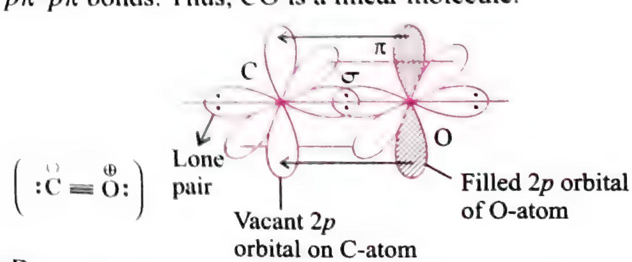
$\boxed{:C=\ddot{O}: \longleftrightarrow :\overset{\ominus}{C}\equiv\overset{\oplus}{O}:}$

Experimental evidence for the presence of triple bond between C and O are as follows:

i. Carbon–oxygen bond length is 113 pm, which corresponds to carbon–oxygen triple bond.

ii. The dipole moment of CO is very low due to back donation of a pair of electrons from the more electronegative O-atom to the less electronegative C-atom.

In CO molecule, both C and O atoms are *sp* hybridised. One *sp*-hybrid orbital from each of C and O overlap to form a (C–O) (σ) bond, while the other *sp*-orbital on both C and O atoms contain the lone pair of electrons. The two unhybridised *p*-orbitals of C and O form two $p\pi$–$p\pi$ bonds. Thus, CO is a linear molecule.



Due to the presence of a lone pair of electrons on the carbon atom, CO acts as a Lewis base or a ligand and form a coordinate bond with metals to form metal carbonyls ($M \longleftarrow :C\equiv O$).

Properties:

1. CO is a colourless and odourless gas.
2. CO is sparingly soluble in water and is a neutral oxide.
3. Reducing agent: Since CO gets easily oxidised to CO_2, it acts as a powerful reducing agent. It reduces almost all metal oxides other than those of alkali and alkaline earth metals, aluminium and a few transition metals. This property of CO is used in the extraction of many metals from their oxide ores.

$$Fe_2O_{3(s)} + 3CO \xrightarrow{\Delta} 3Fe_{(s)} + 3CO_{2(g)}$$

$$ZnO_{(s)} + CO_{(g)} \xrightarrow{\Delta} Zn_{(s)} + CO_{2(g)}$$

$$CuO_{(s)} + CO_{(g)} \xrightarrow{\Delta} Cu_{(s)} + CO_{2(g)}$$

4. Toxic nature: CO is toxic in nature as it reacts with haemoglobin in the blood and forms a complex called carboxyhaemoglobin which is about 300 times more stable than the complex formed by the reaction of oxygen (air) and haemoglobin in the lungs.

Haemoglobin + CO $\longrightarrow$ Carboxyhaemoglobin

Haemoglobin + O_2 $\rightleftharpoons$ Oxyhaemoglobin

This prevents the haemoglobin present in the RBC (red blood cells) from carrying oxygen from the lungs to all parts of the body. This leads to oxygen deficiency causing unconsciousness and ultimately leads to death.

5. Formation of metal cabonyls: In CO molecule, there is one σ and two π bonds between carbon and oxygen ($:\overset{\ominus}{C} \equiv \overset{\oplus}{O}:$).

Because of the presence of lone pair on C, CO acts as a donor and reacts with many metals to form metal carbonyls.

$$Ni + 4CO \xrightarrow{330-350\ K} Ni(CO)_4$$

$$Fe + 5CO \longrightarrow Fe(CO)_5$$

6. CO is an important fuel, because it involves a considerable amount of heat when it burns in air to give a blue flame.

$$2CO + O_2 \longrightarrow 2CO_2 \qquad \Delta \overset{\ominus}{H}_f = -565\ kJ\ mol^{-1}$$

7. CO is quite reactive and combines readily with O, S and halogens F, Cl and Br.

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2$$

$$CO + S \longrightarrow \underset{\text{Carbonyl sulphide}}{COS}$$

$$CO + Cl_2 \longrightarrow \underset{\text{Carbonyl chloride or phosgene}}{COCl_2}$$

7.15.1.2 Carbon Dioxide (CO_2)

Preparation:

1. By complete combustion of carbon and carbon containing fuels in excess of air.

$$C_{(s)} + O_{2(g)} \xrightarrow{\Delta} CO_{2(g)}$$

$$CH_{4(g)} + O_{2(g)} \xrightarrow{\Delta} CO_{2(g)} + 2H_2O_{(l)}$$

2. In laboratory, CO_2 is prepared by the action of dilute mineral acids on carbonates and bicarbonates.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2\uparrow + H_2O$$

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2\uparrow + H_2O$$

3. The main industrial source is as a by-product from the manufacture of hydrogen for making ammonia.

$$CO_{(g)} + H_2O \xrightarrow{\Delta} CO_{2(g)} + H_{2(g)}$$

$$CH_{4(g)} + 2H_2O \xrightarrow{\Delta} CO_{2(g)} + 4H_{2(g)}$$

4. It is also formed during fermentation process in breweries.

$$\underset{\text{Glucose or fructose}}{C_6H_{12}O_6} \xrightarrow[\text{anaerobic conditions}]{\text{Yeast under}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

5. By heating carbonates and bicarbonates of less electropositive metals:

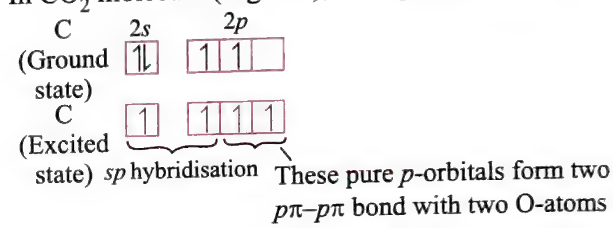
$$ZnCO_3 \longrightarrow ZnO + CO_2\uparrow$$

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

Structure: The electron dot structure for CO_2 molecule may be represented as:

$:\ddot{O}::C::\ddot{O}:$ or $:\ddot{O}=C=\ddot{O}:$

In CO_2 molecule (Fig. 7.9), *C* is *sp* hybridised.



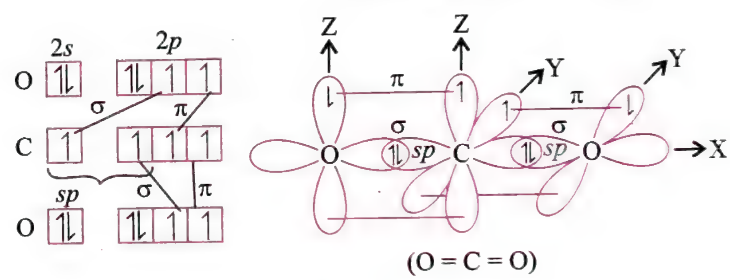


Fig. 7.9 Structure of CO_2 molecule

Two *sp*-hybridised orbitals of C-atom overlap with two *p*-orbitals of O-atoms to make two sigma (σ) bonds, while the other two electrons on C-atoms are involved in $p\pi$–$p\pi$ bonding with O-atoms. As a result, CO_2 is linear, monomeric covalent compound. This structure predicts that C–O bond lengths in CO_2 should be equal and have a typical bond length of 122 pm. But experimentally the bond length was found to be 115 pm only. This can be explained if CO_2 is considered to be resonance hybrid of the following structures.

$$:\overset{\ominus}{\ddot{O}}-C\equiv\overset{\oplus}{O}: \longleftrightarrow :\ddot{O}=C=\ddot{O}: \longleftrightarrow :\overset{\oplus}{O}\equiv C-\overset{\ominus}{\ddot{O}}:$$

Because of resonance, carbon–oxygen bond length acquires some triple bond character; hence, a decrease in bond length from 122 to 115 pm is observed.

Properties:

1. CO_2 is a colourless, odourless and tasteless gas and is about 1.5 times heavier than air.
2. Unlike CO, it is not poisonous in nature. However, it does not support life and animals die in it for want of oxygen.

3. CO_2 is incombustible and non-supporter of combustion. However, some very active metals, e.g. Mg, Na, K etc. continue burning in a jar of CO_2 gas and reduce the gas to elemetary carbon.

$$2Mg + CO_2 \longrightarrow 2MgO + 2C$$

$$4\,Na + CO \longrightarrow 2Na_2O + C$$

4. Acidic nature: CO_2 dissolves in water to form carbonic acid (H_2CO_3) in very small amount, and most of the dissolved CO_2 remains loosely hydrated. CO_2, therefore, is also known as carbonic anhydride.

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(l)}$$

Carbonic acid is a weak dibasic acid, highly unstable and thus cannot be isolated. It forms two series of salts, i.e. hydrogen carbonates and carbonates derived from the anions $HCO_3^{\ominus}$ and CO_3^{2-}.

$$H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons HCO_{3\,(aq)}^{\ominus} + H_3O^{\oplus}_{(aq)}$$

$$HCO_{3\,(aq)}^{\ominus} + H_2O_{(l)} \rightleftharpoons CO_{3\,(aq)}^{2-} + H_3O^{\oplus}_{(aq)}$$

Thus, a solution of CO_2 in water is actually an equilibrium mixture of CO_2, H_2CO_3, $HCO_3^{\ominus}$ and CO_3^{2-}. These equilibria are very important in $H_2CO_3/HCO_3^{\ominus}$ buffer system which helps in maintaining the pH of human blood between 7.26 and 7.42.

5. Photosynthesis: CO_2, which is normally present to the extent of ~ 0.03% by volume in the atmosphere, is removed from it by the process known as photosynthesis. In the presence of chlorophyll (the green colouring pigment of the leaves) and sunlight, the plants absorb CO_2 and react with moisture to form glucose and starch which are used as food by the plant. This process is called photosynthesis.

$$6CO_2 + 6H_2O \xrightarrow[\text{sunlight}]{\text{Chlorophyll}} \underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2\uparrow$$

$$6x\,(CO_2) + 5x\,(H_2O) \longrightarrow \underset{\text{Starch or cellulose}}{(C_6H_{10}O_5)_x} + 6x\,(O_2)\uparrow$$

Photosynthesis is the process by which plants prepare food for themselves as well as for human beings and animals.

6. Reduction: When passed through red-hot coke, it is reduced to carbon monoxide, CO.

$$CO_2 + C \longrightarrow 2\,CO\uparrow.$$

7. Action of lime water: CO_2, when bubbled through lime water, $Ca(OH)_2$, initially turns lime water milky. However, when CO_2 is passed in excess, the solution becomes clear or the milkiness disappears. On heating the clear solution, milkiness reappears. This is explained by the following reactions:

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\substack{\text{Calcium carbonate}\\\text{(insoluble, hence milkiness)}}}{CaCO_3\downarrow} + H_2O$$

$$CaCO_3 + \underset{\text{Excess}}{CO_2} + H_2O \longrightarrow \underset{\substack{\text{Calcium bicarbonate}\\\text{(Soluble, hence milkiness disappears)}}}{Ca(HCO_3)_2}$$

$$Ca(HCO_3)_{2(aq)} \xrightarrow{\text{Heat}} \underset{\substack{\text{Calcium carbonate}\\\text{(Insoluble)}}}{CaCO_3\downarrow} + CO_2\uparrow + H_2O$$

8. Action of NH_3: CO_2 reacts with liquid ammonia (NH_3) at 453–473 K under 220 atm pressure to form ammonium carbonate which subsequently decomposes to give urea.

$$CO_2 + 2NH_3 \xrightarrow[\text{220 atm}]{\text{453–473 K}} \underset{\text{Ammonium carbonate}}{[H_2NCOONH_4]}$$

$$H_2N\,COONH_4 \longrightarrow \underset{\text{Urea}}{H_2NCONH_2} + H_2O$$

9. Solubility: CO_2 is slightly soluble in water. Its solubility in water, however, increases with increase in pressure. Soda water and other aerated soft drinks are, in fact, a solution of CO_2 in water under pressure.

Uses:

1. **As a fire extinguisher:** Air containing ~15% CO_2 does not support combustion. CO_2 is, therefore, used for extinguishing fire.

   a. **Dry powder extinguishers:** It contain sand and baking soda ($NaHCO_3$) which is thrown over the burning fire where $NaHCO_3$ is decomposed by heat and CO_2 is liberated.

   $$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

   b. **Baking soda–sulphuric acid type fire extinguisher:** It contains a bottle of H_2SO_4 supported in a metallic container filled with a strong baking soda solution (Fig. 7.10). On striking the knob, the acid bottle breaks and CO_2 is liberated by the action of H_2SO_4 on baking solid, $NaHCO_3$.

   $$2NaHCO_3 + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + 2CO_2\uparrow + 2H_2O$$

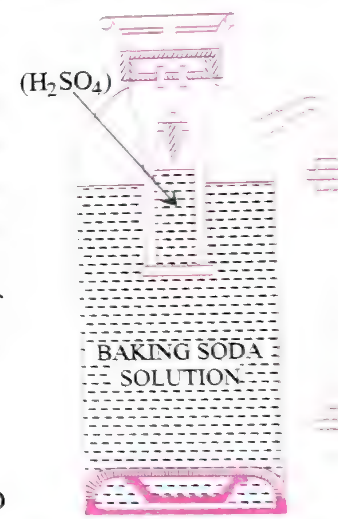


Fig. 7.10 Baking soda–sulphuric acid type fire extinguisher

   c. **Foamite fire extinguishers:** In this, sulphuric acid is replaced by aluminium sulphate, $Al_2(SO_4)_3$, and licorice extract. $Al_2(SO_4)_3$ liberates CO_2 from baking soda and the mixture of $Al(OH)_3$ and licorice acid (a viscous fluid) is blown into flame by CO_2.

   $$Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2SO_4$$

   $$2NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O + CO_2$$

   The foam surrounds the burning object and cuts off supply of air. It has been found to be more effective in extinguishing oil fires which spread instead of being extinguished by water.

2. In the preparation of aerated waters.

3. **Carbogen:** A mixture of 95% O_2 and 5% CO_2 is used for victims of CO poisoning and pneumonia patients in artificial respiration.

4. In the manufacture of washing soda by Solvay ammonia process.
5. Solid CO_2, i.e. *dry ice*, is used as a refrigerant under the commercial name drikold.
6. Supercritical CO_2 is used as a solvent to extract organic compounds from their natural sources such as perfumes from flowers and caffeine from coffee beans.

7.15.1.3 Dry Ice

Solid CO_2 is known as dry ice or cardice or drikold.

Preparation: Dry CO_2 gas is pressurised at 50–60 atm and refrigerated between –57°C and +30°C until it liquefies. Next the pressure is reduced to (~35) atm. As a result some liquid CO_2 vapourises, causing a rapid lowering of the temperature of the remaining liquid. As a result, extreme cold causes liquid to solidify into a snow-like consistency. Finally, the snow-like CO_2 is compressed into either small pellets or larger block of dry ice.

Properties:

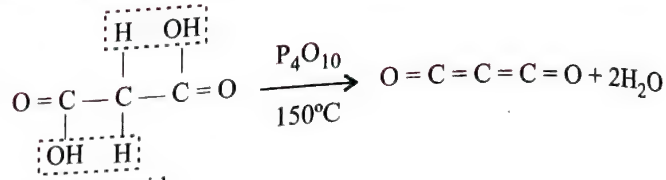
1. Dry ice is a soft, white solid with ρ = 1.53 g cm^{-3}, m.pt. = 216.4 K at 5.2 atm, resembling snow flakes.
2. At pressure below 5.2 atm, if the temperature is raised, it changes into gaseous CO_2 without melting. However, if the pressure is above 5.2 atm, it melts to liquid CO_2 like any other solid.
3. It sublimates very slowly due to low ratio of surface area to volume. As the dry ice sublimates, pressure increases causing the bottle to explode.
4. Dry ice mixed with alcohol, ether or acetone produces intense cooling and can be used as a freezing mixture. For example, temperature of ether–dry ice mixture is as low as 263 K and temperature of acetone–dry ice is 196 K.
5. When the solid CO_2 is kept is air under one atmospheric pressure, it sublimes, i.e. changes directly into the gaseous state without liquifying. As a result, unlike ordinary ice, it does not wet the surface on which it is kept. Therefore, it is called dry ice.

Uses:

1. For making cold baths in the laboratory.
2. For curing local burns.
3. For surgical operation of sores in hospitals.
4. As a refrigerant under the name drikold, in cold drinks and for manufacture of ice cream.
5. In the transport of perishable food-stuffs due to the low temperature and inert atmosphere it produces.
6. Artificial rain is caused by spraying small pellets of dry ice over clouds with the help of aeroplanes.
7. It is used in film industry for creating artificial fogs or clouds.

7.15.1.4 Carbon Suboxide (C_3O_2)

Preparation: By dehydrating malonic acid with P_4O_{10}.



Malonic acid

This reaction shows that C_3O_2 is anhydride of malonic acid.

Properties:

1. C_3O_2 is a foul smelling gas, b.pt. 6°C.
2. Stable at –78°C.
3. Linear molecule.
4. At room temperature, C_3O_2 gas polymerises to a yellow solid and at higher temperatures to red and purple solids.
5. With H_2O, malonic acid is formed.
$C_3O_2 + 2H_2O \longrightarrow HOOC-CH_2-COOH$
6. With HCl, acid chloride is formed.
$C_3O_2 + 2HCl \longrightarrow CH_2(COCl)_2$
7. With NH_3, amide is formed.
$C_3O_2 + 2NH_3 \longrightarrow CH_2(CONH_2)_2$
The other stable carbon suboxide is $C_{12}O_9$. It is a white solid and anhydride of mellitic acid, $C_6(COOH)_6$.

7.15.2 CARBIDES

Binary compounds of carbon with more electropositive elements than itself (except hydrogen) are called carbides.

Thus, this definition excludes the binary carbides of C with N, P, O, S and halogens.

7.15.2.1 General Methods of Preparation

1. By heating metal with C. For example,
   a. $Be + 2C \longrightarrow BeC_2$
   b. $2\,Ag + C \longrightarrow Ag_2C_2$
   c. $3\,Mn + C \longrightarrow Mn_3C$
   d. $2\,Li + C \longrightarrow Li_2C_2$
   e. $3\,Fe + C \longrightarrow Fe_3C$
2. By heating oxides, hydroxides, nitrides, phosphates, sulphates etc. with C. For example,
   a. $MgO + 3C \longrightarrow MgC_2 + CO\uparrow$
   b. $CeO_2 + 4C \longrightarrow CeC_2 + 2CO\uparrow$
   c. $2Al_2O_3 + 9C \longrightarrow Al_4C_3 + 6CO\uparrow$
   d. $SiO_2 + 3C \longrightarrow SiC + 2CO\uparrow$
   e. $U_3O_8 + 14C \longrightarrow 3UC_2 + 8CO\uparrow$
   f. $2Mg(OH)_2 + 4C \longrightarrow 2MgC_2 + 2H_2O + O_2\uparrow$
   g. $Ca_3H_2 + 6C \longrightarrow 3CaC_2 + N_2\uparrow$
   h. $Ca_3(PO_4)_2 + 14C \longrightarrow 3CaC_2 + 2P + 8CO\uparrow$
   i. $4AlPO_4 + 19C \longrightarrow Al_4C_3 + 4P + 16CO\uparrow$
   j. $BaSO_4 + 2C \longrightarrow BaC_2 + SO_2 + O_2\uparrow$
3. By passing acetylene (C_2H_2) or ethylene (C_2H_4) on heated element or its oxide. For example,
   a. $4Li + C_2H_2 \longrightarrow Li_2C_2 + 2LiH$

b. $2Si + C_2H_2 \longrightarrow 2SiC + H_2\uparrow$

c. $2Ag_2O + C_2H_2 \longrightarrow Ag_2C_2 + H_2O$

4. By heating the metallic oxide or halide with CaC_2. For example,

a. $MgO + CaC_2 \longrightarrow MgC_2 + CaO$

b. $CuCl_2 + CaC_2 \longrightarrow CuC_2 + CaCl_2$

c. $MgF_2 + CaC_2 \longrightarrow MgC_2 + CaF_2$

5. By passing CO over metal at high temperature. For example,

a. $2Li + 2CO \longrightarrow Li_2C_2 + O_2\uparrow$

b. $6Al + 3CO \longrightarrow Al_4C_3 + Al_2O_3$

6. By passing acetylene (C_2H_2) through ammonical solution of the metal salt. For example,

a. $2CuCl + 2NH_4OH + C_2H_2 \longrightarrow Cu_2C_2 + 2NH_4Cl + 2H_2O$

b. $2AgNO_3 + 2NH_4OH + C_2H_2 \longrightarrow Ag_2C_2 + 2NH_4NO_3 + 2H_2O$

7. By heating metallic carbonate with C in presence of an oxidisable metal. For example,

$BaCO_3 + C + 3Mg \longrightarrow BaC_2 + 3MgO$

7.15.2.2 General Properties

1. **Crystalline nature:** Generally they are transparent crystalline solids.
2. **Colour:** Carbides of alkali metals and of Ca, Sr and Ba are only colourless while most of the remaining carbides are coloured.
3. **Softness and hardness:** Alkali metal carbides are soft while others are usually hard. For example, Be_2C and UC_2 are so hard that they can scratch glass and quartz.
4. **Explosive nature:** Carbides of U, Cu, Hg(ic) etc. are explosive substance; e.g., Hg(ic) carbides explodes on rapid heating. Uranium carbide emits sparks when struck and takes fire even when powdered quickly.
5. **Reducing property:** The carbides of alkali metals and of Ca, Sr and Ba are strong reducing agents *e.g.*, MgO and $MgCl_2$ are reduced to the metals on heating with CaC_2.

   a. $3MgO + CaC_2 \xrightarrow{\Delta} 3Mg + CaO + CO\uparrow$

   b. $MgCl_2 + CaC_2 \xrightarrow{\Delta} Mg + CaCl_2 + 2C\uparrow$
6. **Hydrolysis:** Ionic carbides can easily be hydrolysed by water or dil acids, with the formation of different types of hydrocarbons.

On the basis of chemical bonding involved, carbides are classified as follows:

1. Ionic or salt-like carbides
2. Covalent carbides
3. Interstitial or metallic carbides
4. Borderline carbides

7.15.2.3 Ionic or Salt-Like Carbides

These are formed by highly electropositive metals of groups 1, 2, 13 (except B), coinage metals, zinc, cadmium and some lanthanides.

They react with water to liberate hydrocarbons.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

Depending on the nature of hydrocarbon liberated on hydrolysis, ionic hydrides are further classified as follows:

1. **Acetylides:** These contain the (acetylide) ion, C_2^{2-} $(C \equiv C)^{2-}$ and liberate acetylene on hydrolysis. CaC_2, which is prepared by the reaction of calcium oxide and carbon at high temperature, reacts with water to liberate acetylene gas, which is used for welding.

   $$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{HC \equiv CH}$$

   BaC_2 and SrC_2 also give C_2H_2 on hydrolysis.
2. **Methanides:** Carbides containing methanide ions, C^{4-}, are called methanides, and they liberate methane (CH_4) gas on hydrolysis, e.g. Be_2C and Al_4C_3.

   $Al_4C_3 + 12H_2O \longrightarrow 12\,Al(OH)_3 + 3CH_4\uparrow$

   $Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4\uparrow$

   Mn_3C probably has related character, since its hydrolysis also gives methane.

   $Mn_3C + 6H_2O \longrightarrow 3Mn(OH)_2 + CH_4 + H_2\uparrow$
3. **Allylides:** One of the two magnesium carbides formed contain allylide ion (C_3^{4-}), and react with water to give allylene and, hence, is known as allylide.

   $$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + \underset{\text{Allylene or propyne}}{H_3C - C \equiv CH}$$
4. **Mixed carbides:** A few carbides like those of Th and U of the formula MC_2 give on hydrolysis, a mixture of several hydrocarbons including acetylene, olefins (alkene) and H_2. These carbides are related in structure to intermetallic compounds.
5. **Structures:** The ionic carbides possess ionic lattices in which the metallic cations are packed into the cavities between carbon anions, e.g. C^{4-}, C_2^{2-} and C_3^{4-}.

7.15.2.4 Covalent Carbides

These are formed by metalloids such as boron and silicon. Boron carbide (B_4C) is harder than silicon carbide and is being used as an abrasive and as protection against radiation. Silicon carbide (SiC) is also known as carborundum.

Properties: These are not attacked by H_2O, dil and conc acids. These are extremely hard and decompose at high temperature. Because of their hardness they are used for cutting and as abrasives.

7.15.2.5 Interstitial or Metallic Carbides

Carbides formed by transition metals belong to this category. They are also called refractory carbides. These carbides are formed by those transition metals whose atomic radii are generally greater than 130 pm, since the radius ratio (r_C/r_M)

must be either 1:0.41 or 1:0.59 to permit C-atom to enter into the octahedral voids of the cubic close packing of the metallic lattice without distorting it. These are two types, viz., MC type (M = Ti, Zr, Hf, V, Nb, Ta, Mo, W) and MC_2 type (M = V, Mo, W).

Some salient features of interstitial carbides are as follows:

1. Higher melting points, e.g. m.pt. of TaC = 4175 K.
2. These are very hard, e.g. WC is used for cutting and drilling tools on account of its hardness. Their hardness on Moh's scale is in the range 9–10.
3. Their crystal lattice is close packed type with carbon atoms occupying the octahedral holes (interstitial voids) in the metal lattice. The presence of carbon, therefore, does not affect the electrical conductivity of the metal.
4. These carbides are chemically inert and extremely hard.
5. These carbides possess metallic lusture and high electrical conductivity which increases at lower temperature and may become infinite at absolute zero.
6. They are weakly paramagnetic which is characteristic of the presence of metal lattice in their crystal structure.
7. They are attacked by strong oxidising agents at red heat.
8. Carbides of Mo and W are somewhat more reactive than the metals from which they are derived but other carbides are less reactive than the parent metals.

7.15.2.6 Borderline Carbides

Fe, Mn, Co, Ni and Cr have atomic radii less than 130 pm (Mn is exception) and hence octahedral voids in the metallic lattice of these metals are too small to accommodate C-atoms in them without producing a great deal of distortion in the metallic lattice. Here the metallic lattice is distorted and these carbides are intermediate in properties between the ionic and interstitial carbides but their radius ratio (r_C/r_M) is in the range of 60–61 pm, which place these carbides closer to the interstitial carbides.
Properties: They are relatively less stable and liberate a mixture of hydrocarbons and H_2 on hydrolysis with H_2O or acids.

7.15.3 FUEL

Any combustible substance which on burning produces heat energy without the production of excessively undesirable product is known as a fuel.

7.15.3.1 Requisite of a Good Fuel

1. It should have high calorific value.
2. It should produce very little ash content.
3. It should not give any offensive odour or any undesirable product during combustion.
4. It should be cheap and easily available.
5. The combustion should be of moderate speed.

7.15.3.2 Different Types of Fuel

1. **Solid fuels:** These are derived from plants directly or indirectly. These include wood, coal, coke, charcoal etc.
2. **Liquid fuels:** Petroleum products (e.g. petrol, kerosene etc.) and alcohols. These are more convenient and leave no solid ash.
3. **Gaseous fuels:** Combustible gases such as coal gas, water gas etc. make excellent fuels. Gaseous fuels are the best fuels.

Gaseous fuel	Main components	Composition
Coal gas	–	H_2 (56%), CH_4 (22.8%), CO (10.9%), O_2 (0.5%), CO_2 (1.3%), N_2 (5.0%), C_2H_2, C_2H_4, benzene (2.5%)
Water gas	CO and H_2	CO (40–50%), H_2 (44–50%), CO_2 (3–7%), N_2 (4–5%)
Producer gas	CO + N_2	CO (30–40%), N_2 (50%), H_2 (2–5%), some CO_2
Oil gas	Mixture of lower hydrocarbons	—
Natural gas	CH_4	CH_4 (85%), C_2H_6 (9%), C_3H_8 (3%), C_4H_{10} (1%), N_2 (2%)
LPG	*n*-butane, isobutane	—
Biogas	CH_4	CH_4, CO, H_2, CO_2, H_2S, N_2 etc.

7.15.4 CARBON–NITROGEN COMPOUNDS

Some important compounds of carbon and nitrogen are as follows.

7.15.4.1 Calcium Cyanamide ($CaCN_2$) {Ca^{2+} $[N=C=N]^{2-}$}

Preparation: It is obtained by heating finely powdered calcium carbide (CaC_2) with a little of $CaCl_2$ in the atmosphere of CO_2 at 1000 – 1100°C in an electric furnace. $CaCl_2$ accelerates the rate of reaction.

$$CaC_2 + N_2 \xrightarrow[1000-1100°C]{CaCl_2} \underbrace{\underset{\text{Calcium cyanamide}}{CaNCN} + \underset{\text{Carbon}}{C}}_{\text{Nitrolim}}$$

It is usually obtained as a dark grey mass. Grey colour is due to the presence of carbon. The grey mass which is a mixture of calcium cyanamide and carbon is used as a nitrogenous fertiliser. Its trade name is *Nitrolim*.

Properties:

1. Pure $CaCN_2$ forms colourless, rhombohedral crystals which sublime at 1300°C, without melting.
2. Reaction with superheated steam:

$$CaCN_2 + \underset{\text{Superheated steam}}{3H_2O} \longrightarrow CaCO_3 + 2NH_3$$

This reaction is used for the manufacture of NH_3 on a large scale by cyanamide process.

3. Reaction with coke:

$$CaCN_2 + C \xrightarrow{\text{Fusion}} \underset{\text{Calcium cyanide}}{Ca(CN)_2}$$

4. Reaction with NaCl or Na_2CO_3: Crude calcium cyanamide (i.e. a mixture of calcium cyanamide and coke) on heating with NaCl or Na_2CO_3 produces NaCN.

$$CaCN_2 + 2NaCl + C \longrightarrow CaCl_2 + 2NaCN$$

$$CaCN_2 + C + 2Na_2CO_3 \longrightarrow CaCO_3 + 2NaCN$$

This reaction is used to prepare sodium cyanide (NaCN). Sodium cyanide is used for the extraction of gold and silver from their ores. Treatment of NaCN with strong acids liberate HCl which is a colourless gas and behaves as a weak acid in aqueous solution ($pK_a = 9.0$). Industrially, HCN is obtained by the reaction of ammonia with methane at a high temperature.

$$CH_4 + NH_{3(g)} \xrightarrow[\text{1500 K}]{\text{Pt catalyst}} HCN_{(g)} + 3H_{2(g)}$$

Cyanides and HCN are extremely poisonous substances. Ingestion or inhalation can lead to instant death. HCN is used in the manufacture of methylmethacrylate polymers and adiponitrile, which is an intermediate for nylon.

Uses:

1. Nitrolim acts as a good nitrogenous fertiliser. When added to soil, it first changes into calcium carbonate and cyanamide.

$$CaCN_2 + H_2O + CO_2 \longrightarrow \underset{\text{Calcium carbonate}}{CaCO_3} + \underset{\text{Cyanamide (m.pt. 318 K)}}{H_2N{\cdot}CN}$$

The cyanamide then hydrolyses in two stages to give ammonia as the final product.

$$H_2N{\cdot}CN + H_2O \longrightarrow \underset{\text{Urea}}{H_2NCONH_2}$$

$$H_2NCONH_2 + H_2O \longrightarrow CO_2\uparrow + 2NH_3$$

Ammonia is converted into nitrates through the agency of nitrifying bacteria. On account of its slow conversion into ammonia and nitrates, calcium cyanamide is a valuable fertiliser as its effects are of prolonged nature. The formation of $CaCO_3$ in the process in also useful from agricultural point of view.

2. It is used for the manufacture of melamine plastics.

7.15.4.2 Cyanogen $(CN)_2$

Cyanogen was discovered by Gay-Lussac in 1815. Cyanogen has a superficial resemblance to halogens (X_2) and is referred to as **pseudohalogen.**

Preparation:

1. Cyanogen is produced by the oxidation of HCN by O_2 using a silver catalyst.

$$4HCN + O_2 \longrightarrow 2(CN)_2 + 2H_2O$$

2. By oxidation of potassuim cyanide by $CuSO_4$ solution. The reaction proceeds as follows:

$$CuSO_4 + 2KCN \longrightarrow K_2SO_4 + Cu(CN)_2$$

$$2Cu(CN)_2 \longrightarrow 2CuCN + (CN)_2$$

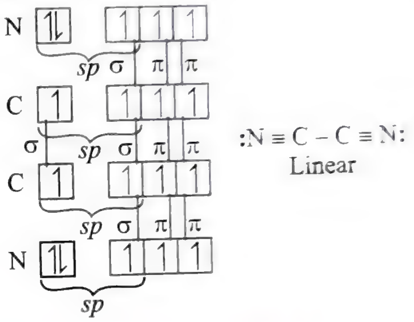
or

$$2Cu^{2+} + 4CN^{\ominus} \longrightarrow 2CuCN + (CN)_2$$

Properties:

1. It is colourless, extremely poisonous, flammable gas. (b.pt. = $-21.2°C$)
2. It has smell of bitter almonds.
3. It burns in air to give a violet colourless flame. This reaction is explosive in nature.
$$(CN)_2 + 2O_2 \longrightarrow 2CO_2 + N_2$$
4. It disproportionates in basic solution to give cyanide and cyanate ions.
$$(CN)_2 + 2KOH \longrightarrow KCN + KCNO + H_2O$$
or
$$(CN)_2 + 2\overset{\ominus}{O}H \longrightarrow CN^{\ominus} + OCN^{\ominus} + H_2O$$

Structure: In $(CN)_2$, both C and N are *sp*-hybridised.



7.15.5 Carbonic Acid (H_2CO_3)

An aqueous solution of carbon dioxide behave as a weak acid, which is due to the formation of carbonic acid.

$$CO_2 + H_2O \rightleftharpoons \underset{\text{Carbonic acid}}{H_2CO_3}$$

This is why CO_2 is also known *carbonic anhydride*.

Carbonic acid is known only in the solution and has not been isolated in the free state.

It is a weak dibasic acid and ionises in two steps:

$$H_2CO_3 \rightleftharpoons H^{\oplus} + HCO_3^{\ominus}$$

$$HCO_3^{\ominus} \rightleftharpoons H^{\oplus} + CO_3^{2-}$$

Since H_2CO_3 is a weak dibasic acid, its structure has two –OH groups directly linked to the central C atom. The structure of H_2CO_3 has been inferred from that of the metallic carbonates.

The carbonate ion, CO_3^{2-}, is coplanar (bond angle: 120°) and is considered to be a resonance hybrid of the canonical forms as shown in Fig. 7.11.

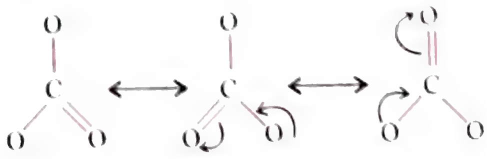


Fig. 7.11 Resonance hybrid of CO_3^{2-} ion

The three carbon–oxygen bonds are having the same bond length, which means that each bond has one-third double bond character.

The carbon atom in CO_3^{2-} ion is sp^2 hybridised due to which the bond angle is 120°.

7.15.5.1 Carbonates and Bicarbonates

Carbonic acid is a dibasic acid and gives rise to two series of salts:

1. Carbonates, i.e. normal salts. These contain CO_3^{2-} ion.
2. Bicarbonates, i.e., acid salts. These contain $HCO_3^{\ominus}$ ion.

The metallic carbonates and bicarbonates are prepared as follows:

a. By passing CO_2 through an alkali.

$$2NaOH + CO_2 \longrightarrow Na_2CO_3\downarrow + H_2O$$

$$\underset{\text{Excess}}{Na_2CO_3 + CO_2} + H_2O \longrightarrow \underset{\text{(Soluble)}}{2NaHCO_3}$$

The carbonate formed first changes to bicarbonate on excess passage of CO_2.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O$$

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$

b. By precipitation: Heavy metal carbonates are precipitated from the salt solutions with washing soda

$$Na_2CO_3 + BaCl_2 \longrightarrow BaCO_3\downarrow + 2NaCl$$

c. By reacting basic oxides and CO_2.

$$K_2O + CO_2 \longrightarrow K_2CO_3$$

$$Na_2O + CO_2 \longrightarrow Na_2CO_3$$

Properties:

S.No.	Property	Carbonates	Bicarbonates
1.	Solubility	Except alkali metal carbonates, all the carbonates are insoluble in water.	Bicarbonates are solube in water. Bicarbonates of alkali metal are known in the solid state, all other bicarbonates exist only in the solution state.
2.	Action of heat	Alkali metal carbonate, except Li_2CO_3, do not decompose on heating. All other carbonates decompose on heating to give CO_2. $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2\uparrow$ $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2\uparrow$ $CuCO_3 \xrightarrow{\Delta} CuO + CO_2$ $Ag_2CO_3 \xrightarrow{\Delta} 2Ag + CO_2 + \frac{1}{2}O_2$	All the bicarbonates decompose on heating to give CO_2. $MHCO_3 \xrightarrow{\Delta} M_2CO_3 + CO_2\uparrow + H_2O$ e.g., $Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + CO_2 + H_2O$ The carbonates formed further decomposes except alkali metal carbonates. $M_2CO_3 \longrightarrow MO + CO_2$ e.g., $CaCO_3 \longrightarrow CaO + CO_2\uparrow$
3.	Action of acids	Carbonates are decomposed by acids with effervescene due to evolution of CO_2. $CaCO_3 + HCl \longrightarrow CaCl_2 + CO_2\uparrow + H_2O$	Bicarbonates are decomposed by acids with effervescence due to evolution of CO_2. $CaHCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$
4.	Reaction with $MgSO_4$*	Soluble carbonates give a white ppt. with magnesium sulphate in cold. $Na_2CO_3 + MgSO_4 \longrightarrow Na_2SO_4 + \underset{\text{white ppt.}}{MgCO_3\downarrow}$	Bicarbonates do not form any white ppt. with $MgSO_4$ in cold. However, on heating a white ppt. is formed. $2NaHCO_3 + MgSO_4 \longrightarrow \underset{\text{(Soluble)}}{Mg(HCO_3)_2} + Na_2SO_4$ $Mg(HCO_3)_2 \xrightarrow{\Delta} \underset{\text{White ppt.}}{MgCO_3\downarrow} + CO_2 + H_2O$
5.	Hydrolysis	Being salt of weak acid, carbonates undergo hydrolysis The solution is alkaline and gives a pink colour with phenolphthalein. $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^{\ominus} + H^{\oplus}$ — (1) $HCO_3^{\ominus} + H_2O \rightleftharpoons H_2CO_3 + \overset{\ominus}{O}H$ — (2) Although it also undergoes ionisation to a small extent, according to following reaction $HCO_3^{\ominus} \rightleftharpoons CO_3^{2-} + H^{\oplus}$ — (3) $(2) + (3) \Rightarrow 2HCO_3^{\ominus} \rightleftharpoons H_2CO_3 + CO_3^{2-}$	Being salt of weak acid, bicarbonates undergo hydrolysis. The solution is alkaline but it does not give a pink colour with phenolphthalein, which suggests that carbonates are stronger bases as compared to bicarbonates. *Hydrolysis* : $HCO_3^{\ominus} + H_2O \rightleftharpoons H_2CO_3 + \overset{\ominus}{O}H$ *Ionisation* : $HCO_3^{\ominus} \rightleftharpoons CO_3^{2-} + H^{\oplus}$

* $MgSO_4$ is the reagent by which carbonates and bicarbonates can be distinguished.

7.15.5.2 Interconversion of Carbonates and Bicarbonates

Consider an equation: $2\,HCO_3^{\ominus} \rightleftharpoons H_2CO_3 + CO_3^{2-}$. This equation explains the interconversion of carbonates and bicarbonates in aqueous solution. When CO_2 is passed into an aqueous solution of a carbonate or its suspension in water, the equilibrium shifts in the backward direction and a bicarbonate is formed. On the other hand, when the solution of bicarbonate is boiled, CO_2 is given off, thus moving the equilibrium in the forward direction and carbonate is produced. A bicarbonate can also be converted into a carbonate by treatment with an alkali which neutralises carbonic acid.

7.15.6 SILICON TETRACHLORIDE ($SiCl_4$)

It is also known as tetrachlorosilane.

Preparation: By passing dry Cl_2 over:

1. Heated silicon: $Si + 2Cl_2 \longrightarrow SiCl_4$
2. Heated magnesium silicide:

   $Mg_2Si + 4Cl_2 \longrightarrow SiCl_4 + 2MgCl_2$
3. A red hot mixture of silica and charcoal:

   $SiO_2 + 2C + 2Cl_2 \longrightarrow SiCl_4 + 2CO$

Structure: It is tetragonal, sp^3 hybridised with 109.4° angle.

Properties:

1. It is a colourless fuming liquid; b.pt. 330 K.
2. It is a covalent compound.
3. Hydrolysis: $SiCl_4$ gets easily hydrolysed to form silicic acid, $Si(OH)_4$, which on further heating undergoes partial dehydration to give silica gel. $SiCl_4$ easily gets hydrolysed as Si can increase its coordination number from 4 to 5 due to the availability of vacant low lying *d*-orbitals in its valence shell. Thus, $SiCl_4$ coordinates with the lone pair on O-atom of water molecule to attain its covalency of 5. This coordination compound breaks up with the elimination of HCl molecule.

   The process of addition of H_2O molecule and elimination of HCl continues till all the –Cl group in $SiCl_4$ are replaced by the –OH group. The mechanism of hydrolysis of $SiCl_4$ is represented in Fig. 7.12. The hydrolysis proceeds via S_N2 (substitution nucleophilic bimolecular) mechanism.

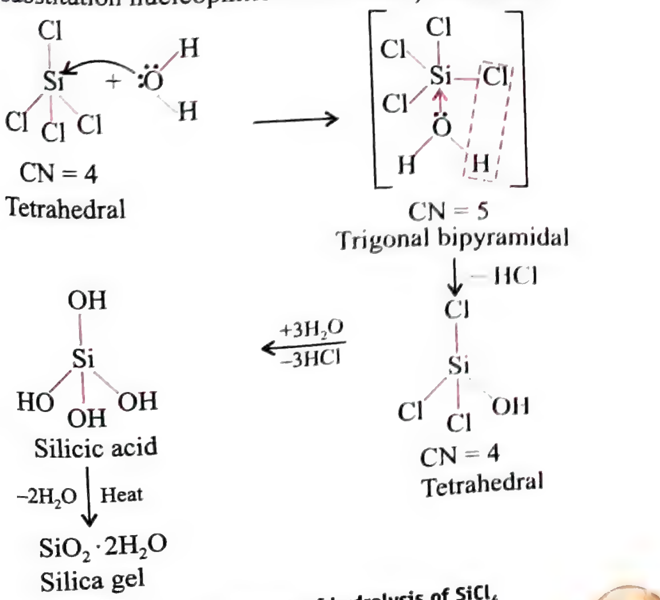


Fig. 7.12 Mechanism of hydrolysis of $SiCl_4$

On the other hand, CCl_4 does not undergo hydrolysis due to the absence of vacant *d*-orbitals in its valence shell, it cannot expand its coordination number beyond 4 and hence cannot coordinate with water molecule.

Silica gel is amorphous and very porous. It contains about 4% water. It is used as a catalyst in petroleum industry and as an absorbent in column chromatography.

If hydrolysis of $SiCl_4$ is carried out at high temperature (in an oxy-hydrogen flame) instead of $Si(OH)_4$, finely powdered silica is obtained.

$$SiCl_{4(g)} + 4H_2O_{(l)} \xrightarrow[O_2-H_2\text{ flame}]{\text{High temp.}} SiO_{2(s)} + 4HCl_{(g)}$$

The ultrafine silica thus obtained is used as

a. A thixotropic agent (the property of showing a temporary reduction in viscosity when shaken or stirred is called *thixotropy*) in polyester and epoxy paints and resins.

b. As an inert filler in silicon rubber.

4. With silicon: Pyrolysis, i.e. strong heating of $SiCl_4$ with Si gives a series of perhalosilanes of the general formula Si_nCl_{2n+2}, where $n = 2 - 6$.

   $SiCl_4 + Si \xrightarrow{\Delta} Si_2Cl_6 + Si_3Cl_8 + Si_4H_{10} + Si_5H_{12} + Si_6H_{14}$

   These chains are longer than formed by silanes, i.e. hydrides of Si due to additional $p\pi$–$d\pi$ bonding between lone pairs of electrons present on Cl and empty 3*d* orbital of Si.
5. Reduction: Reduction of $SiCl_4$ with H_2 gives Si.

   $SiCl_4 + 2H_2 \xrightarrow{\Delta} Si_{(s)} + 4HCl_{(g)}$

   This reaction is used to make ultrapure silicon, which is required for making transistors, computer chips and solar chips. For this purpose, impure Si is first converted into $SiCl_4$ by reacting with Cl_2. $SiCl_4$ thus formed is then separated by distillation. Subsequent reduction of pure $SiCl_4$ with H_2 gives silicon.

7.15.7 CARBORUNDUM (SiC)

Silicon carbide is the chemical name of carborundum.

Preparation: It is obtained when a mixture of sand, carbon, common salt and saw dust is strongly heated in an electric furnace.

$SiO_2 + 3C \longrightarrow SiC + 2CO$

Common salt acts as a flux and saw dust makes the mass porous. Two carbon rods connected by a thin carbon core act as electrodes in the furnace. Carborundum is formed around the central core of the carbon. It is crushed, washed with H_2SO_4, NaOH, H_2O and then dried.

Properties:

1. Pure carborundum is colourless but commercial products show tint of yellow, blue or green.
2. It is very hard. However, its hardness is less than diamond.
3. It is chemically inert and is not attacked by even HF. However, it decomposes when fused with alkalis, forming soluble silicates and carbonates.

   $4NaOH + SiC + 2O_2 \longrightarrow \underbrace{Na_2SiO_3 + Na_2CO_3}_{\text{(Soluble)}} + 2H_2O$

4. Its structure is similar to that of diamond.

Uses:

1. As an abrasive for cutting and grinding glass.
2. It is used for making grinding wheels, knife, sharpeners etc. When it is mixed with moistened china clay and feldspar and moulded under pressure, it results in a fired kiln.
3. As a preservative for eggs.
4. As a filler in soap industry.
5. In paint industry and calico printing.
6. As an adhesive for joining pieces of china clay.
7. For making silica gel, $SiO_2 \cdot xH_2O$: On acidification of a solution of Na_2SiO_3 with HCl, a gelatinous precipitate of silicic acid, H_2SiO_3, is slowly formed.

   $Na_2SiO_3 + 2HCl \longrightarrow 2NaCl + H_2SiO_3$

   On carefully removing most of the water, the jelly-like precipitate of H_2SiO_3 is converted into a solid product, which is known as silica gel. Silica gel possesses excellent absorption property of gases and vapours.

7.15.8 Silicon Dioxide (SiO_2)

Silicon dioxide is commonly known as silica. Ninety-five percent of the earth's crust is made up of silica and silicates. Silica occurs in many crystallographic forms such as quartz, crystobalite and tridymite. These are interconvertible at suitable temperatures.

	(Low temperature forms)	
α-Quartz	α-Tridymite	α-Crystobalite
$\rightleftharpoons$ 846 K	$\rightleftharpoons$ 395–435 K	$\rightleftharpoons$ 475–550 K
β-Quartz $\xrightleftharpoons{1140\text{ K}}$	β-Tridymite $\rightleftharpoons$	β-Crystobalite
		$\rightleftharpoons$ 1985 K
	(High temperature forms)	Liquid silica

Amorphous forms of silica are: Agate, Jaspar and Onyx.

Sand is the crushed form of quartz, which is produced in nature by the weathering of rocks.

Sandstone consists of sand particles bound together with iron oxide.

Flint consists of amorphous silica associated with quartz.

Kieselguhr is a siliceous rock composed of the remains of minute sea organisms. It is used as an absorbent for nitroglycerine and as a polishing powder.

Silica is also diffused into plant and animal kingdoms. It is present in considerable amount in stems and exterior coating of straw and bamboo, quills of feathers, claws of animals, finger nails etc.

Two important amorphous forms of silica are (i) silica gel and (ii) Kieselguhr.

Structure of SiO_2: Silicon dioxide (Fig. 7.13) is a covalent. Si–O bonds have considerable iónic character due to large EN difference between Si and O. As a result silica has three-dimensional network solid in which each silicon atom is bonded to four oxygen atoms which are arranged tetrahedrally around it and each oxygen atom is attached to two silicon atoms by covalent bonds. Each corner is further shared by another tetrahedron.

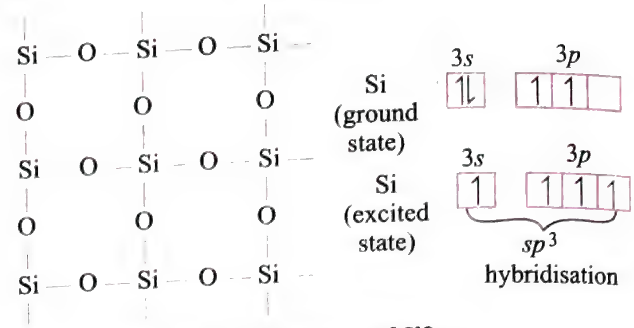


Fig. 7.13 Structure of SiO_2

There is no discrete molecule but the entire crystal may thus be considered as a giant molecule in which eight-membered rings are formed with alternate silicon and oxygen atoms.

Properties:

1. As Si–O bonds are very strong (368 kJ mol^{1-}), silica is relatively inert and has a very high melting point.
2. It does not react with halogens (except F_2), dihydrogen and most of the acids (except HF) and metals even at high temperatures.

   With F_2: $SiO_2 + 2F_2 \longrightarrow \underset{\text{Silicon tetrafluoride}}{SiF_4} + O_2\uparrow$

   With HF: It is readily attacked by HF, resulting in the formation of SiF_4.

   $SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$

   SiF_4 thus formed dissolves in HF, forming hydroflurosilicic acid.

   $SiF_4 + 2HF \longrightarrow H_2SiF_6$

   Due to the formation of H_2SiF_6, SiO_2 present in glass dissolves. Therefore, HF cannot be stored in glass bottles. HF is stored in copper or monel metal alloy (32% Cu + 68% Ni + traces of Fe).
3. Silica is insoluble in water but dissolves in water to a small extent when heated under pressure above 385 K.
4. Silica dissolves in hot alkali solution to form soluble silicates.

   $SiO_2 + 2NaOH \longrightarrow \underset{\text{Sodium silicate}}{Na_2SiO_3} + H_2O$

   $SiO_2 + Ca(OH)_2 \longrightarrow \underset{\text{Calcium silicate}}{CaSiO_3} + H_2O$
5. At high temperatures, silica acts as a powerful acid anhydride and combines with bases and many metallic oxides to form silicates.

   $SiO_2 + Na_2O \longrightarrow Na_2SiO_3$

   It also reacts with many metal carbonates at high temperatures, forming silicates with the liberation of carbon dioxide.

$SiO_2 + Na_2CO_3 \longrightarrow Na_2SiO_3 + CO_2\uparrow$

$SiO_2 + CaCO_3 \longrightarrow CaSiO_3 + CO_2\uparrow$

The above reactions show that SiO_2 behave as an acidic oxide.

6. When heated with carbon in an electric furnace, SiO_2 is reduced to silicon carbide or carborundum.

$SiO_2 + 3C \longrightarrow SiC + 2CO$

7. Silica melts in oxy-hydrogen flame at 1875 K to form a colourless glass known as quartz glass. It has remarkably low coefficient of expansion. Red hot quartz when plunged in water does not shatter to pieces. On account of this property, quartz glass is used to manufacture chemical apparatus and optical instruments. The specific gravity of quartz or rock crystal is 2.65 g cm^{-3}, while that of tridymite and cristobalite is 2.25 g cm^{-3} and 2.32 g cm^{-3}, respectively.

7.15.8.1 Silica Gel

Preparation:

1. By the action of water on silicon tetrafluoride or tetrachloride.

$$\underset{}{SiCl_4} + 4H_2O \longrightarrow \underset{\text{Silica gel}}{SiO_2{\cdot}2H_2O} + 4HCl$$

2. By the action of acid (HCl) on soluble sodium silicate white gelatinous precipitate of silica gel is obtained.

$$Na_2SiO_3 + 2HCl + H_2O \longrightarrow SiO_2{\cdot}2H_2O + 2NaCl$$

3. By dehydrating silicic acid

$$\underset{\text{Silicic acid}}{Si(OH)_{4(aq)}} \longrightarrow SiO_2{\cdot}2H_2O$$

Silica gel is amorphous and very porous. It contains about 4% water and is used as follows:

a. As a catalyst in petroleum industry and as an absorbent in column chromatography.
b. Silica gel is frequently stained with $(NH_4)_2CoCl_4$, a humidity detector that is pink when hydrated and blue when dry. To protect merchandise from moisture during storage, small packets of dry silica gel (blue) are placed in the packing boxes.

7.15.8.2 Kieselguhr

It is a porous white powder and is used as follows:

1. In filtration plants
2. As an abrasive
3. As an inert support or filler, e.g.
   a. Dynamite is a mixture of glyceryl trinitrate and glyceryl dinitrate absorbed on kieselguhr.
   b. Gelignite is a mixture of explosive nitrobenzene (liquid) and kieselguhr (solid).

7.15.9 SILICATES

Introduction

Silicates are alumino-silicates of magnesium, calcium, iron etc. Quartz, mica, feld spar and zeolites are important examples of silicates. These are found in almost all rocks, clays and soils present in earth's crust. Glass and cement are two most useful silicates, which are the man-made silicates.

General properties of silicates

Silicates are of various types. Excepting Na_2SiO_3, which is soluble in water, all other silicates are insoluble in water. Si—O bond in silicates is very strong. This bond can be broken when silicates are treated with strong reagents like HF. Although Si—O bond is covalent, it has appreciable degree of ionic character. Ionic character is due to the fact that the electronegativity difference between oxygen and silicone atoms is equal to 3.5 – 1.8 = 1.7.

Structure and types of silicates

The structure of silicates has been found with the help of X-ray diffraction techniques. All silicates have tetrahedral SiO_4^{4-} ion, as a basic building unit, i.e., all silicates are composed of many units. Tetrahedral shape of SiO_4^{4-} ion is due to sp^3 hybridization of Si-atom, in its excited state.

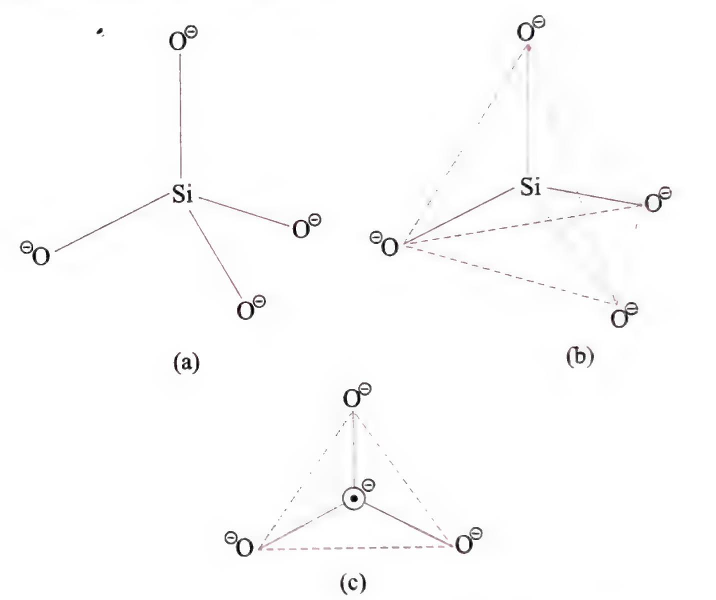
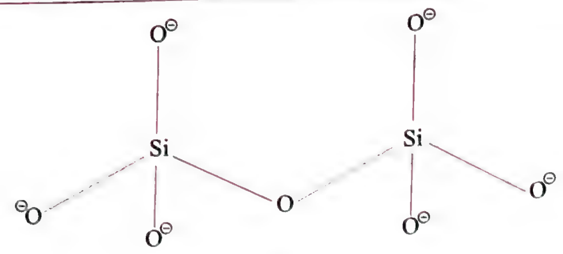


Fig. 7.14 Various ways of representing tetrahedral shape of SiO_4^{4-} ion. In (c) white circles represents O-atoms and black circle represents Si-atom

Tetrahedral shape SiO_4^{4-} ion can be represented by any of the three figures shown in Fig. 7.14. In representation (c), the white circles represent O-atoms and small black circle represents Si-atom.

They are classified depending upon the number of corners (0, 1, 2, 3 or 4) of the SiO_4^{4-} tetrahedral shared with other tetrahedral.

1. **Orthosilicates:** These are simple silicates and contain discrete orthosilicate (SiO_4^{4-}) ions, since these ions do not share O-atoms with one another. Examples of orthosilicates are *zircon* ($ZrSiO_4$), *wellimite* (Zn_2SiO_4), *phenacite* (Be_2SiO_4) and *garnets* $[M_3^{2+}M_2^{3+}(SiO_4)_3]$ where $M^{2+} = Ca^{2+}$, Mg^{2+} or Fe^{2+} and $M^{3+} = Al^{+3}$, Cr^{+3} or Fe^{3+}.
2. **Pyrosilicates or islands:** The basic unit in these silicates in pyrosilicate ion, $Si_2O_7^{6-}$. This ion is formed when two SiO_4^{4-} tetrahedrons share one O-atom (bridging O-atom), i.e., in this ion one O-atom acts as a bridge between two Si-atoms. The structure of this ion is shown in Fig. 7.15



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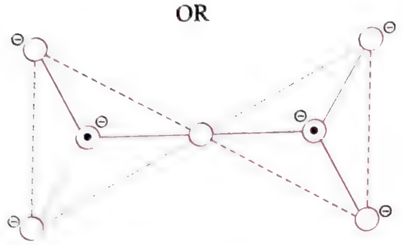


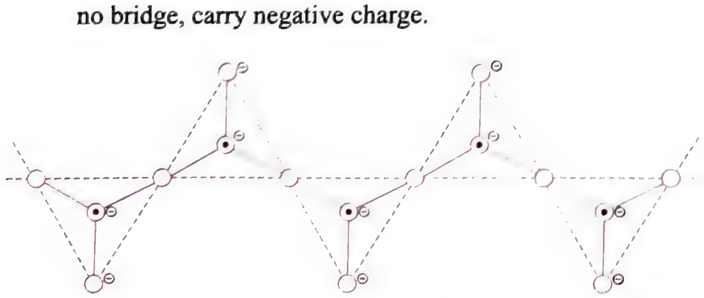
Fig. 7.15 Structure of pyrosilicate ion, $Si_2O_7^{6-}$

This structure shows that each Si-atom is surrounded by $3+\frac{1}{2}=3.5$ oxygen atoms: Thus the basic unit found in these silicates can be represented as $[SiO_{3.5}]^{3-}$ or $Si_2O_7^{6-}$ ion.

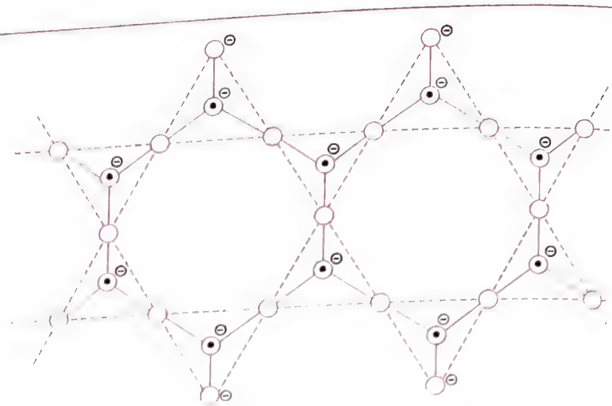
It may be noted from the structure of $Si_2O_7^{6-}$, ion that O-atom, which is shared by two SiO_4^{4-} units, does not carry any charge on it. O-atoms, forming no bridges between SiO_4^{4-} tetrahedrons, have negative charge. This negative charge is produced because each of these O-atoms picks up an electron from some metal. Examples of pyrosilicates are *thortveitite* ($Sc_2Si_2O_7$) and *hemi-morphite* $[Zn_4(OH)Si_2O_7]$.

3. **Chain silicates:** These silicates are of two types viz., *single chain silicates* and *double chain silicates*. Single chain silicates contain $[(SiO_3)_n]^{-2n}$ ion as the primary unit, while double chain silicates contain $[(Si_4O_{11})_n]^{-6n}$ as the primary unit. The structure of these ions is shown at (a) and (b) respectively of Fig. 7.16. $[(SiO_3)_n]^{-2n}$ ion is obtained when each tetrahedron shares two O-atoms (bridging O-atoms). $[(Si_4O_{11})_n]^{-6n}$ ion is formed by further sharing of O-atom by half the Si-atom.

   It may be noted that O-atoms, which are shared by SiO_4^{4-} tetrahedrons, do not contain any negative charge, i.e., O-atoms, forming a bridge between SiO_4^{4-} tetrahedral units, do not carry any negative charge. O-atoms, forming no bridge, carry negative charge.



(a) Structure of $[(SiO_3)_n]^{-2n}$ ion

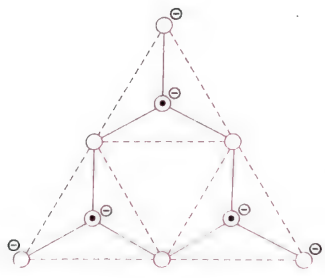


(b) Structure of $[(Si_4O_{11})_n]^{-6n}$ ion

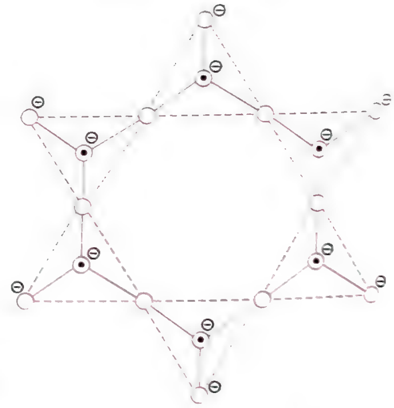
Fig. 7.16 Structure of $[(SiO_3)_n]^{-2n}$ and $[(Si_4O_{11})_n]^{-6n}$ ions which are the basic units of chain silicates.

Common examples of single chain silicates are the minerals *pyroxenes*, like *enstatite* ($MgSiO_3$), *diopside* $[CaMg(SiO_3)_2]$ and *spodumene* $[LiAl(SiO_3)_2]$. Common examples of double chain silicates are the minerals *amphiboles*, like *tremolite* $[Ca_2Mg_5(Si_4O_{11})_2(OH)_2]$, *crocidolite* $[Na_2Fe_3^{2+}Fe_2^{3+}(Si_4O_{11})_2(OH)_2]$ etc.

4. **Cyclic or ring silicates:** These silicates have cyclic structure and contain $[(SiO_3)_n]^{-2n}$ ion as the primary unit. These silicates are formed when each SiO_4^{4-} tetrahedron shares two O-atoms (bridging O-atoms). The structure of cyclic ions viz., $[(SiO_3)_3]^{-6}$ or $Si_3O_9^{-6}$ and $[(SiO_3)_6]^{-12}$ or $Si_6O_{18}^{-12}$ ions are shown at (a) and (b) respectively of Fig. 7.17.



(a) Structure of $[(SiO_3)_3]^{-6}$ or $Si_3O_9^{-6}$ ion



(b) Structure of $[(SiO_3)_6]^{-12}$ or $Si_6O_{18}^{-12}$ ion

Fig. 17.17 Structure of $Si_3O_9^{6-}$ and $Si_6O_{18}^{-12}$ ions

$Si_3O_9^{6-}$ ion is found in *wollastonite* $[Ca_3Si_3O_9]$ and *bentonite* $[BaTiS_3O_9]$, and $Si_6O_{18}^{-12}$ ion occurs in *beryl* ($Be_3Al_2Si_6O_{18}$).

5. **Silicates having sheet or layered structure: Sheet silicates:** These silicates are formed when three O-atoms (bridging O-atoms) of each SiO_4^{4-} unit are shared. This type of sharing gives an infinite two-dimensional layered structure to the silicates (Fig.7.18). $[(Si_2O_5)_n]^{-2n}$ ion is the basic unit of sheet silicates. In Fig. 7.18. O-atom, shown round Si-atom of each SiO_4^{4-} tetrahedron carries a negative charge, while the remaining three O-atoms, which act as bridging O-atoms, do not carry this charge.

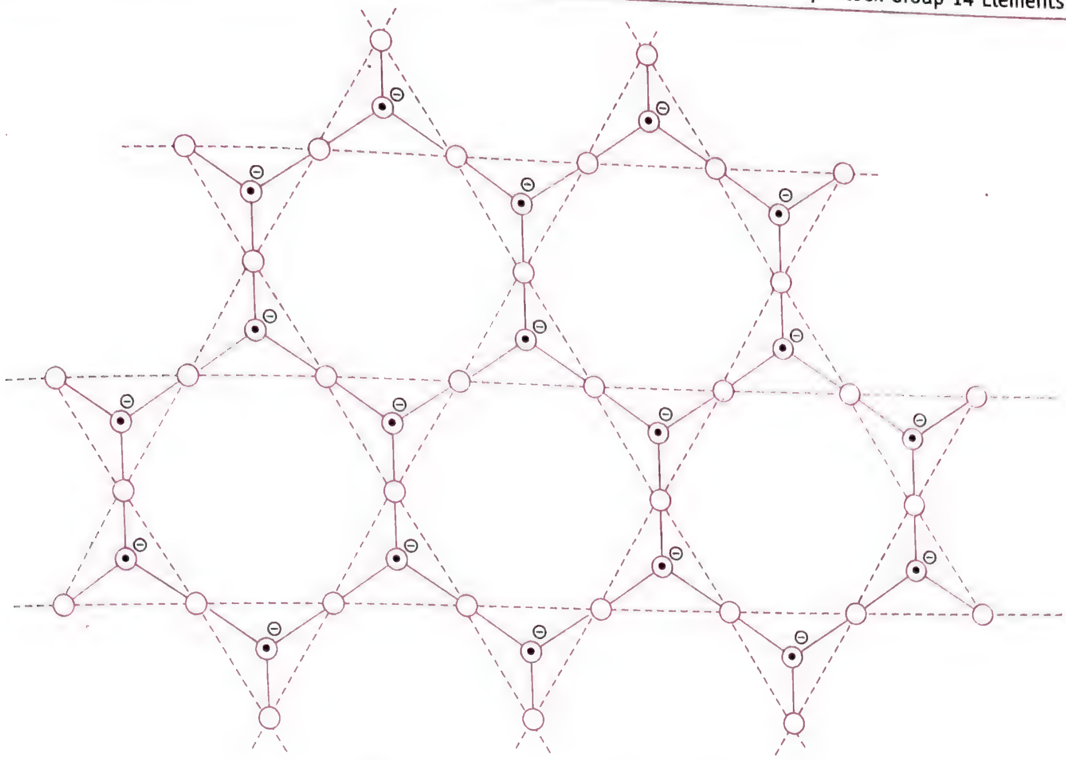


Fig. 7.18 Structure of sheet silicates

Negative charge on non-bridging O-atom is neutralized by the positive charge on the cations, which lie in between the sheets.

Examples of silicates having layered structure are given below. These are generally *aluminio silicates*.

(i) *Clays*. These are produced by weathering and decomposition of igneous rocks. They are generally composed of very fine particle. *Kaoline* (which is a china clay) is formulated as $Al_2O_3.2SiO_2.2H_2O$ or $Al_2(OH)_4Si_4O_5$ and has a sheet-structure, in which the sheets are held together by OH bridges.

When clay is mixed with water, it becomes plastic-soft and mouldable. Water of plasticity can be removed by heating at 100°C. Clay becomes rigid and brittle when water of plasticity has been eliminated. On heating beyond 100°C, structural water of crystallisation is removed and carbonaceous matter of the clay gets oxidised. At about 900°C, *multite* ($Al_6Si_2O_{13}$) begins to be formed. This new substance has *glassy appearance*. Clay is widely used in making chinaware, fire bricks and many other useful materials.

(ii) *Talc*. It is formulated as $Mg_3(OH)_2(Si_4O_{10})$, which consists of electrically neutral sheets and has no cations in between them. It is soft and smooth. It is chemically inert. It is used as a dry lubricant, in ceramics, paper manufacture and cosmetics.

(iii) *Muscovite*, $KAl_2(OH)_2(Si_3AlO_{10})$. Muscovite is an example of mica. It is obtained when one Si-atom in $Si_4O_{10}{}^{4-}$ ion is replaced by Al-atom. Thus we see, that in muscovite, the sheet composition is $(Si_3AlO_{10})^{5-}$. Two $(Si_3AlO_{10})^{5-}$ sheets, which have tetrahedral vertices inward, are linked by binding Al^{3+} cation, whose octahedral coordination is completed by OH^- ions. The double sheets, which have the composition, $[Si_3Al_3O_{10}(OH)_2]^-$, are stacked one upon another with sufficient number of K^+ cations. These cations are located in between two such double sheets and maintain electrical neutrality. The cleavage of mica is due to the weakening of these layers of K^+ ions. The binding Al^{3+} ions and the sandwiched K^+ ions can be replaced by Mg^{2+} and Na^+ ions respectively.

Micas are often tough, elastic and transparent. These are chemically inert, stable towards heat and have high dielectric constant. They are used in furnace windows and electrical appliances. The powdered mica is used as a filler for rubbers, plastics and in insulation boards.

6. **Silicates having three dimensional structure:** In these silicates, all the four O-atoms act as bridging atoms, i.e., in these silicates, each $SiO_4{}^{4-}$ tetrahedron shares all its four O-atoms with other $SiO_4{}^{4-}$ tetrahedron. This type of sharing gives three-dimensional silicates, corresponding to the composition SiO_2 (*quartz, tridymite* or *crystobalite*). The replacement of Si^{4+} ions by a combination of Al^{3+} and other cations (to maintain electrical neutrality) gives minerals known as *feldspars*, *zeolites* and *ultramarines*.

Feldspars: These are also aluminio silicates. Almost 67% of the igneous rocks are composed of feldspars minerals. These have been grouped into two categories namely (i) *Orthoclase feldspars*. Examples are *orthoclase* ($KAlSi_3O_8$), *celsian* ($BaAl_2Si_2O_8$) etc. (ii) *Plagioclase feldspars*. Examples are *albite* ($NaAlSi_3O_8$), *anorthite* ($CaAl_2Si_2O_8$) etc.

Orthoclase feldspars are more symmetrical than plagioclase feldspars, because the cations viz., K^+ and Ba^{2+} present in them are of the right size to fit into the lattice. On the other hand in plagioclase feldspars the cations Na^+ and Ca^{2+} are smaller and hence produce distortion.

Summary

1. Pyrosilicates: $(Si_2O_7^{6-})$	1-corner O-atom/T.H. is shared. Each Si atom is surrounded by $\left(3+\frac{1}{2}\right) = 3.5$ oxygen atom.
2. Single chain silicates: $[(SiO_3)_n]^{2n-}$	2-corner O-atom/T.H. is shared. [one T.H. shares 3corners while other adjacent one shares only 2-corners hence average shared corners $= \frac{3+2}{2} = 2.5$] Each Si atom is surrounded by 2.5 oxygen atom.
3. Double chain silicates: $[(Si_4O_{11})_n]^{6n-}$	One T.H. shares 2 corners O-atoms while one T.H. shares 3 corners O-atoms. These two T. H. constitute one unit. $\therefore$ Average shared corners $= \frac{2+3}{2} = 2.5$
4. Cyclic silicates $[(SiO_3)_n]^{2n-}$ $Si_3O_9^{6-}$, $Si_6O_{18}^{12-}$	2 corner O-atom/T.H. is shared.
5. Sheet silicates $[(Si_2O_5)_n]^{2n-}$	3 corner O-atoms are shared
6. 3D silicates	4 corner O-atoms are shared

a. **Feldspars:** It is the most abundant of all the minerals, and almost 67% of the igneous rocks consist of feldspar minerals. These are usually classified as:

Orthoclase feldspars

Examples:	Orthoclase	$KAlSi_3O_8$
	Celsian	$BaAl_2Si_2O_8$

Plagioclase feldspars

Examples:	Albite	$NaAlSi_3O_8$
	Anorthite	$CaAl_2Si_2O_8$

Orthoclase feldspars are more symmetrical than plagioclase feldspars because the cations $K^{\oplus}$ and Ba^{2+} present in them are of right size to fit into the lattice. Plagioclase feldspars contain cations such as $Na^{\oplus}$ and Ca^{2+} which are smaller in size and permit distortion.Egyptian blue ($CaCuSi_4O_{10}$) is an example of sheet silicates.

b. **Zeolites:** As compared to feldspars, zeolites have a more open structure, which permits the formation of channels and cavities of different size ranging from 2.11 to 4.3 Å in diameter. Water molecule and a variety of other molecules such as NH_3, CO_2 and C_2H_5OH can be trapped in these channels or cavities. Thus, zeolites act as ion exchangers and as molecular sieves. A number of zeolites are manufactured industrially and are used as water softeners. They trap Ca^{2+} ions from hard water and replace them by $Na^{\oplus}$ ions.

Zeolites may be represented by the general formula: $M_{x/n}[(AlO_2)_x)(SiO_2)_y]\cdot zH_2O$

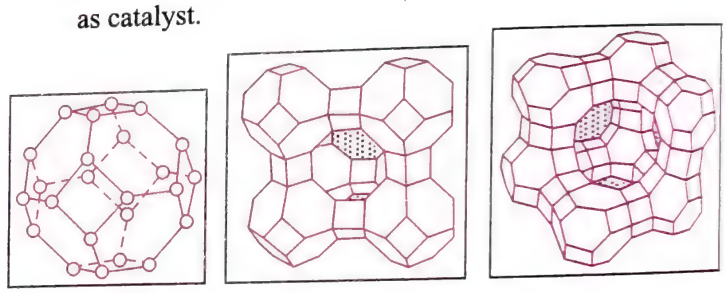
where M is the metal cation such as $Na^{\oplus}$, $K^{\oplus}$ or Ca^{2+}; n is the charge on the metal cation; and z is the number of moles of water molecule of crystallisation.

The negative charge of the aluminosilicate framework is neutralised by exchangeable cations of valency n. The void space, which can be greater than 50% of the volume, is occupied by m molecules of water in the unit cell. The truncated octahedron (cubo-octahedron) (a) is the building block of zeolites. This is also called the b-cage or sodalite cage.

Zeolites have high porosity due to the presence of one-, two- or three-dimensional network of interconnected channels and cavities of molecular dimensions.

Accordingly, zeolite shown as in (b) is formed by linking sodalite cages through double four-membered rings. Faujasite is formed by linking the sodalite cages through double six-membered rings (c).

Zeolites are used as molecular sieves and can separate molecules of different sizes. They are also used extensively as catalyst.



(a) (b) (c)

Examples:

Zeolite	Formula
Erionite	$Na_2K_2CaMg(AlO_2)_2(Si\ O_2)_6\cdot 6H_2O$
Gemelinite	$Na_2Ca(AlO_2)_2\ (SiO_2)_4\cdot 6H_2O$
Chabazite	$Na_2Ca(AlO_2)_2(SiO_2)_4\cdot 6H_2O$

Molecular sieves can be made with pores of approximate size to remove small molecules selectively.

c. **Ultramarines:** Ultramarines do not contain water. Moreover, some extra anions such as $Cl^{\ominus}$, S_2^{2-} and SO_4^{2-} may also be present in the cavities. Many of the ultramarines are coloured and are used as *pigments*.

Examples:

Sodalite	$Na_8(AlO_2)_6(SiO_2)_6Cl_2$
Ultramarine	$Na_8(AlO_2)_6(SiO_2)_6S_2$
Nosean	$Na_8(AlO_2)_6(SiO_2)_6SO_4$

Now ultramarines are synthetically produced. Ultramarine is made by igniting kaolinite, sodium carbonate and sulphur in the absence of air. The product may be green, blue or red depending on the polysulphide species present.

7.15.10 SODIUM SILICATE (Na_2SiO_3)

Chemically, sodium silicate is sodium metrasilicate containing an excess of silica. Its composition may vary from $Na_2SiO_3 \cdot SiO_2$ to $Na_2SiO_3 \cdot 3SiO_2$. Its chemical name is water glass.

Preparation: By fusing soda ash (Na_2CO_3) with pure sand (SiO_2) at high temperature.

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2\uparrow$$

The resulting mass is extracted with water and the solution is evaporated to get a syrupy mass known as water glass.

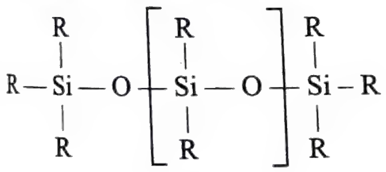
Properties:

1. Sodium silicate is soluble in water. Its aqueous solution is alkaline due to hydrolysis.
   $$Na_2SiO_3 + H_2O \rightleftharpoons 2NaOH + H_2SiO_3$$
2. If in a solution of sodium silicate ($\rho = 1.1$ g cm^{-3}), some coloured salts such as cobalt nitrate, nickel chloride, ferrous sulphate, copper sulphate etc. are placed, and the whole solution is left as such overnight, beautiful hollow tubes of metallic silicate gels possessing different colours shoot up from these crystals, which look like plants. This is known as silica garden or chemical garden.

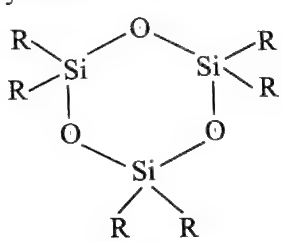
Uses: In fireproofing of wood and textiles.

7.15.11 SILICONES OR SILICON POLYMERS

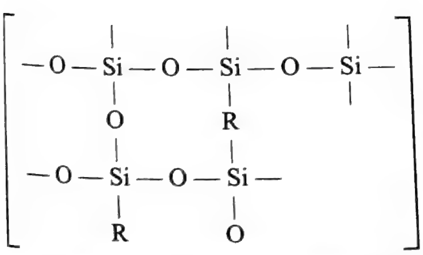
1. Silicones are polymeric organosilicon compounds having Si – O – Si linkages. These compounds have the general formula $(R_2SiO)_x$, where R is alkyl or aryl group. They may be linear, cyclic or cross-linked polymers.



Linear



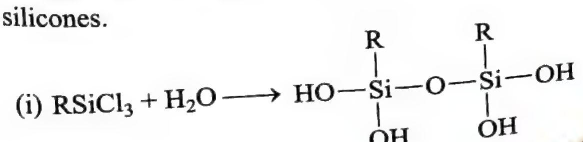
Cyclic

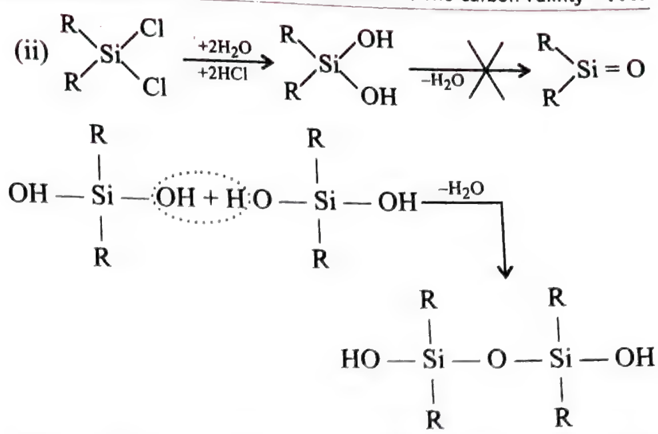


Branched or cross-linked

Since their empirical formula R_2SiO is similar to that of ketone R_2CO, the name silicone has been given to these materials.

2. The complete hydrolysis of $SiCl_4$ yields SiO_2, which has a very stable three-dimensional structure. The fundamental research of F. S. Kipping on hydrolysis of alkyl-substituted chlorosilanes led not to the excepted silicon compound analogous to a ketone but to a long-chain polymer called silicones.

(i) 

(ii) 

This led to the formation of a wide range of organosilicon polymers.

3. **Preparation:** Industrial synthesis of silicones was carried out by E.G. Rochow in 1945.

   Hydrolysis of alkyl- or aryl-substituted silicon halides followed by condensation produces silicones. The halogen derivatives are themselves made by passing aryl halide or alkyl halide over a copper–silicon alloy at about 570 K.

4. **Hydrolysis of $(CH_3)_3$Si-Cl gives a disiloxane.**

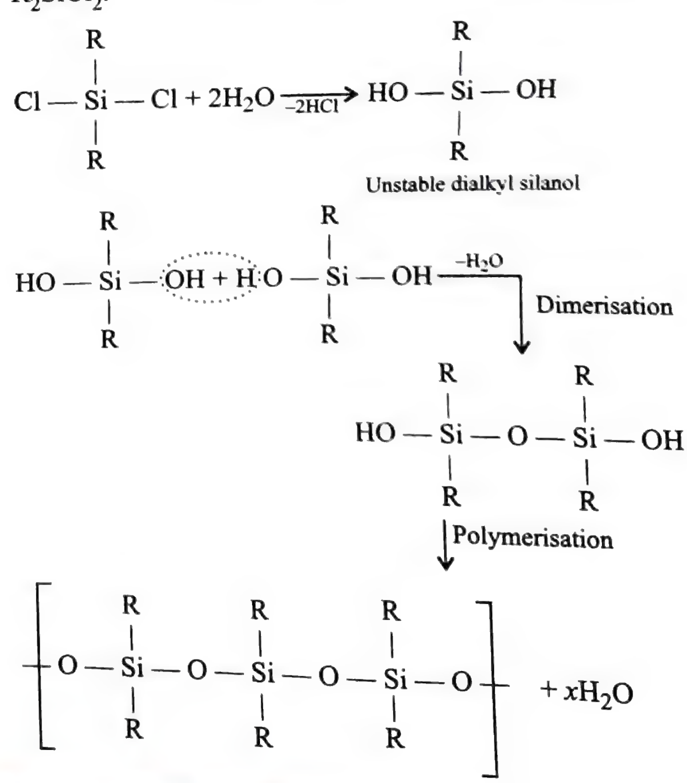
$$2RCl + Si \xrightarrow[570\ K]{Cu\ Powder} R_2SiCl_2$$

$$(CH_3)_3Si\text{–}Cl + H_2O \longrightarrow \underset{\text{Trimethylsilanol}}{(CH_3)_3Si\text{–}OH} + HCl$$

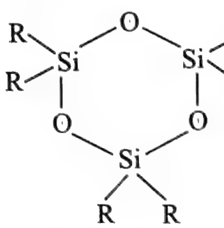
$$\underset{\text{Volatile liquid}}{(CH_3)_3Si\text{–}OH + H\text{–}O\text{–}Si(CH_3)_3} \xrightarrow[\text{Condensation}]{-H_2O} \underset{\text{Hexamethyldisiloxane}}{(CH_3)_3Si\text{–}O\text{–}Si(CH_3)_3}$$

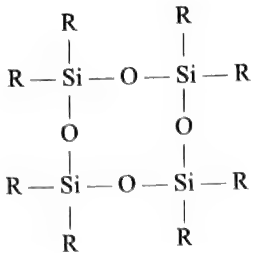
Since hexamethyldisiloxane has no –OH group, it cannot polymerise any further.

5. **Linear silicones** can be obtained by the hydrolysis and subsequent condensation of dialkyl or diaryl silicon chloride, R_2SiCl_2.



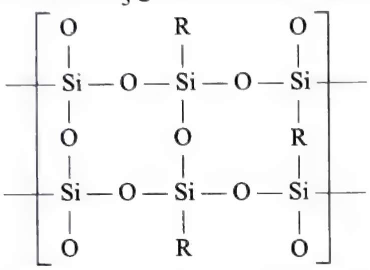
6. Hydrolysis under carefully controlled condition can produce *cyclic* structures, with rings containing three, four, five or six Si atoms.





Tricyclodimethylsiloxane   Tetrakis cyclodimethyl siloxane

7. Hydrolysis of $RSiCl_3$ gives a *cross-linked* chain system.



8. If some R_3SiCl is mixed with R_2SiCl_2 and hydrolysed, then R_3SiCl will block the end of straight chain produced by R_2SiCl_2. Since there is no longer a functional OH-group at the end of the chain, it cannot grow any more on that end. Eventually, the other end is blocked by this way. Thus, R_3SiCl and R_2SiCl_2 in the starting material will decide the average chain length. By controlled mixing of the reactants, any given type of polymer can be produced.

9. **Properties and uses:**
   a. Depending on the chain length, silicones may be liquids, oils, greases, rubbers (elastomers) or resins. As the chain length increases, viscosity increases and the nature of the silicones changes from liquid to oil to grease to rubbers (elastomers) or resins.
   b. Boiling point and viscosity of silicone increase with chain length. Viscosity of silicone oil remains constant with change in temperature and as such do not thicken in cold weather. Hence, they are better lubricant or grease as compared to graphite at high as well as low temperature.
   c. Silicones are fairly stable and inert. Their strength and inertness is related to
      i. Si–O–Si linkage. The Si–O bond energy is very high (503 kJ mol^{-1}).
      ii. High strength of Si–C bond.

      Silicones are resistant to heat. Most heat stable side groups are phenyl groups followed by methyl, ethyl, propyl groups in descending order of stability. Silicone are resistant to oxidation and to most chemicals. As a result,

      - *Silicones act as good electrical insulators* because they are more stable to heat than organic polymers, and even if they do break down, they do not produce conducting material as carbon does. They can withstand high temperature without charring.
      - Silicones show non-stick and antifoaming properties.

   d. Silicones being surrounded by non-polar groups such as alkyl or aryl are water repelling in nature. Because of their water repellant nature, they are used to treat building glasswares and fabrics and in car and shoe polish.
   e. Being biocompatible, they are used in surgical and cosmetic implants.

7.15.12 Hydrated Stannous Chloride ($SnCl_2 \cdot 2H_2O$)

It is also known as tin salt.

Preparation: By dissolving tin in hot and conc HCl and subjecting the solution to crystallisation.

$Sn + 2HCl \longrightarrow SnCl_2 + H_2$

Properties:

1. It exists as transparent monoclinic crystal, with m.pt. 40°C.
2. On heating hydrated stannous chloride, $SnCl_2 \cdot 2H_2O$, it undergoes hydrolysis, resulting in the formation of tin hydroxy chloride, a white solid.

   $SnCl_2 \cdot 2H_2O \xrightarrow{\Delta} Sn(OH)Cl + HCl + H_2O$

   Hence, anhydrous stannous chloride cannot be obtained by heating hydrated stannous chloride.
3. It dissolves in small quantity of water. But, when water is in excess, it undergoes hydrolysis.

   $$\underset{}{SnCl_2} + \underset{\text{Excess}}{H_2O} \longrightarrow \underset{\substack{\text{Tin hydroxychloride}\\ \text{(white ppt.)}}}{Sn(OH)Cl\downarrow} + HCl$$

   However, in the presence of HCl, hydrolysis is reversed.
4. With alkalis: White ppt. of stannous hydroxide is formed. which dissolves in excess of alkali to form sodium stannite, Na_2SnO_2, which further reacts with atmospheric O_2 to form Na_2SnO_4.

   $SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2\downarrow + 2NaCl$

   $$Sn(OH)_2 + 2NaOH \longrightarrow \underset{\substack{\text{Sodium stannite}\\ \text{(soluble)}}}{Na_2SnO_2} + 2H_2O$$

   $$2Na_2SnO_2 + O_2 \longrightarrow \underset{\text{Sodium stannate}}{2Na_2SnO_4}$$
5. With H_2S: On passing H_2S gas through aqueous solution of stannous chloride, yellow precipitate of SnS is formed. SnS dissolves in yellow ammonium sulphide $[(NH_4)_2S + S]$.

   $SnCl_2 + H_2S \longrightarrow SnS + 2HCl$

   $$SnS + (NH_4)_2S + S \longrightarrow \underset{\text{Ammonium thiostannate}}{(NH_4)_2SnS_3}$$
6. It acts as a good reducing agent. It reduces $Fe^{3+} \rightarrow Fe^{2+}$; $Hg^{2+} \rightarrow Hg^{\oplus}$, $Hg^{\oplus} \rightarrow Hg$, $Cu^{2+} \rightarrow Cu^{\oplus}$

   - $$\overset{(+3)}{2FeCl_3} + \overset{(+2)}{SnCl_2} \longrightarrow \overset{(+2)}{2FeCl_2} + \overset{(+4)}{SnCl_4}$$

- $\overset{(+2)}{2HgCl_2} + \overset{(+2)}{SnCl_2} \longrightarrow \overset{(+1)}{Hg_2Cl_2} + \overset{(+4)}{SnCl_4}$
- $\overset{(+1)}{Hg_2Cl_2} + \overset{(+2)}{SnCl_2} \longrightarrow \underset{\text{Grey ppt.}}{\overset{(0)}{Hg}\downarrow} + \overset{(+4)}{SnCl_4}$
- $\overset{(+2)}{2CuCl_2} + \overset{(+2)}{SnCl_2} \longrightarrow \underset{\text{White ppt}}{\overset{(+1)}{Cu_2Cl_2}\downarrow} + \overset{(+4)}{SnCl_4}$
- It reduces gold chloride to metallic gold.

$$2AuCl_3 + 3SnCl_2 \longrightarrow \underset{\text{Colloidal gold}}{2Au} + 3SnCl_4$$

$SnCl_2$ undergoes hydrolysis to form stannic acid, which absorbs colloidal particles of gold, thus forming purple of cassius.

Uses:

1. For making *purple of cassius*, which is used for colouring glass and pottery.
2. As a mordant in dyeing.
3. As a reducing agent.

7.15.13 Anhydrous Stannous Chloride ($SnCl_2$)

Preparation:

1. By passing dry HCl gas over hot tin.

$$Sn + \underset{\text{Dry}}{HCl} \longrightarrow SnCl_2 + H_2\uparrow$$

2. By heating a mixture of Sn with a calculated amount of mercuric chloride.

$$Sn + HgCl_2 \longrightarrow SnCl_2 + Hg$$

Properties:

1. It is a white crystalline solid.
2. It is a covalent compound and soluble in organic solvents such as alcohol and ether.
3. With NH_3: It combines with ammonia to form a number of addition compounds, depending on the temperature of the reaction.

Temperature	Addition compound
<0°C	$SnCl_2{\cdot}2NH_3$
At ordinary temperature	$SnCl_2{\cdot}2NH_3$ and $SnCl_2{\cdot}NH_3$
100°C	$SnCl_2{\cdot}NH_3$
>100°C	$3SnCl_2{\cdot}2NH_3$(most stable)

Uses:

1. As a mordant in dyeing, under the name tin salt.
2. As a reducing agent.
3. In the preparation of *purple of cassius*.

7.15.14 Stannic Chloride ($SnCl_4$)

Preparation:

1. By passing dry Cl_2 over molten tin kept in a retort.

$$Sn + 2Cl_2 \longrightarrow SnCl_4$$

$SnCl_4$, which is a volatile, is collected in a water cooled receiver protected from atmospheric moisture by a calcium chloride guard tube.

2. By heating Sn with excess of $HgCl_2$.

$$Sn + 2HgCl_2 \xrightarrow{\Delta} SnCl_4 + 2Hg$$

Properties:

1. It is a colourless, fuming liquid with a disagreeable smell.
2. It is a covalent compound, as indicated by: (a) its volatile nature, (b) solubility in organic solvent such as benzene (c) very negligible electrical conductivity.
3. In small amount of water, $SnCl_4$ dissolves with the evolution of heat and forms a clear solution, from which several soluble hydrate can be crystallised, e.g. $SnCl_4{\cdot}3H_2O$, $SnCl_4{\cdot}5H_2O$, $SnCl_4{\cdot}6H_2O$ etc. The penta hydrate, $SnCl_4{\cdot}5H_2O$ is known as butter of tin or oxymuriate of tin.
4. In excess of water, it undergoes hydrolysis.

$$SnCl_4 + 4H_2O \longrightarrow Sn(OH)_4 + 4HCl$$

5. With conc HCl, it forms soluble chlorostannic acid. In the presence of NH_4Cl, it forms ammonium salt of this acid.

$$SnCl_4 + 2HCl \longrightarrow \underset{\text{Chlorostannic acid}}{H_2SnCl_6}$$

$$H_2SnCl_6 + 2NH_4Cl \longrightarrow \underset{\text{Ammonium chlorostannate}}{(NH_4)_2SnCl_6}$$

Uses:

1. $SnCl_4{\cdot}5H_2O$ is used as a mordant; in ammonium chlorostannate form, it is used as a mordant for pink dyes.
2. For increasing the weight of silk.
3. For fireproofing cotton.

7.15.15 Lead Monoxide (PbO)

It occurs in two forms:

1. A yellow powder commonly known as massicot.
2. A buff-coloured crystalline form known as litharge.

Preparation:

1. By heating lead or lead sulphide in air, at 3000°C, massicot. is formed, whereas at 900°C, litharge is formed.

$$2Pb + O_2 \longrightarrow 2PbO$$

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

2. By heating lead nitrate or lead carbonate.

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2\uparrow + O_2\uparrow$$

$$PbCO_3 \xrightarrow{\Delta} PbO + CO_2\uparrow$$

Properties:

1. It is insoluble in water.
2. It behaves as an amphoteric oxide, i.e. it dissolves in both acids and alkalis.

$$PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$$

$$PbO + 2NaOH \longrightarrow Na_2PbO_2 + H_2O$$

3. On heating in air at 470°C, red lead is formed.

$$6PbO + O_2 \longrightarrow \underset{\text{Red lead}}{2Pb_3O_4}$$

Uses:

1. For making glass, paints and varnishes.
2. A mixture of massicot and glycerine is used as a cement for glass and pottery.
3. For making other lead compounds.

7.15.16 Lead Suboxide (Pb_2O)

It is obtained by heating lead oxalate in absence of air.

$$2PbC_2O_4 \xrightarrow{\Delta} Pb_2O + 3CO_2 + CO$$

7.15.17 Lead Dioxide (PbO_2) or Peroxide of Lead

1. It is obtained as a chocolate brown powder when red lead is treated with nitric acid.

$$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2$$

2. In the laboratory it is generally prepared by the oxidation of lead salt with bleaching powder which contains some slaked lime too.

$$(CH_3COO)_2Pb + Ca(OH)_2 \longrightarrow Pb(OH)_2 + (CH_3COO)_2\,Ca$$

$$Pb(OH)_2 + \underset{\text{Bleaching powder}}{CaOCl_2} \longrightarrow PbO_2 + CaCl_2 + H_2O$$

Properties:

1. It is powerful oxidising agent, gives O_2 on heating alone or with conc. H_2SO_4.
   a. $2PbO_2 \longrightarrow 2PbO + O_2$
   b. $2PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O + O_2$
2. It oxidises HCl to Cl_2:
   $PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$
3. It dissolves in cold conc. HCl forming $PbCl_4$.
   $PbO_2 + 4HCl \longrightarrow PbCl_4 + 2H_2O$
4. It dissolves in hot, concentrated solution of alkalis forming plumbates.
   $PbO_2 + 2NaOH \longrightarrow \underset{\text{Sodium plumbate}}{Na_2PbO_3} + H_2O$

Uses: In storage cells and in match industry as an oxidising agent.

7.15.18 Lead Sesquioxide (Pb_2O_3)

It is obtained as a yellowish red powder by heating PbO to 775 K in air.

$$4PbO + O_2 \xrightarrow[\Delta]{} 2Pb_2O_3$$

It is similar in behaviour to red lead (Pb_3O_4).

7.15.19 Red Lead or Lead Tetraoxide (Pb_3O_4)

Red lead is also known as **minium or *sindoor*.**

Preparation: By heating litharge (PbO) at 470°C in air.

$$6PbO + O_2 \xrightarrow{470°C} 2Pb_3O_4$$

Properties:

1. It is a red powder, insoluble in water.
2. On heating, it becomes almost black, but on cooling again, it becomes red.
3. On heating above 470°C, it decompose into PbO and O_2.
   $Pb_3O_4 \longrightarrow 3PbO + \frac{1}{2}O_2$
4. With conc HNO_3
   $Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$
   In this reaction, both lead nitrate, $Pb(NO_3)_2$, and brownish black insoluble residue PbO_2 are produced, which indicates that Pb_3O_4 is a compound oxide containing both 2PbO and PbO_2 in the ratio 2:1.
5. With H_2SO_4
   $2Pb_3O_4 + 6H_2SO_4 \longrightarrow 6PbSO_4 + 6H_2O + O_2\uparrow$
6. It acts as an oxidising agent
   $Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$
   $Pb_3O_4 + 4C \longrightarrow 3Pb + 4CO$
   $Pb_3O_4 + 4CO \longrightarrow 3Pb + 4CO_2$

Uses:

1. As a red pigment.
2. As an oxidising agent in match industry.
3. In glass industry.
4. For making protective paint for iron and steel.

7.15.20 Lead Acetate $(CH_3COO)_2Pb$

It is also known as sugar of lead.

Preparation: By dissolving lead oxide (litharge) or lead carbonate or basic lead carbonate in acetic acid (45%) and crystallising the solution.

$$PbO + 2CH_3COOH \longrightarrow (CH_3COO)_2Pb + H_2O$$

$$PbCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Pb + CO_2 + H_2O$$

$$2PbCO_3{\cdot}Pb(OH)_2 + 6CH_3COOH \longrightarrow 3(CH_3COO)_2Pb + 2CO_2 + 4H_2O$$

Properties:

1. White crystalline solid.
2. It is soluble in water, and its solution is sweet in taste. For this reason, it is known as *sugar of lead*. However, it is poisonous in nature.
3. On heating, it decomposes to give acetone.
   $(CH_3COO)_2Pb \xrightarrow{\Delta} PbO + CO_2\uparrow + \underset{\text{Acetone}}{CH_3COCH_3}$
4. With $NaHCO_3$:
   $(CH_3COO)_2Pb + 2NaHCO_3 \longrightarrow \underset{\text{Lead carbonate (White ppt.)}}{PbCO_3\downarrow} + 2CH_3COONa + CO_2 + H_2O$
5. With Na_2CO_3:
   $3(CH_3COO)_2Pb + 3Na_2CO_3 + H_2O \longrightarrow \underset{\text{Basic lead carbonate}}{2PbCO_3{\cdot}Pb(OH)_2} + 6CH_3COONa + CO_2$

6. With H_2S: When H_2S gas is passed through the solution of $(CH_3COO)_2Pb$, black ppt. of PbS is formed.

$$(CH_3COO)_2Pb + H_2S \longrightarrow 2CH_3COOH + \underset{\text{Black ppt.}}{PbS\downarrow}$$

$$Pb^{2+} + S^{2-} \longrightarrow \underset{\text{Black ppt.}}{PbS\downarrow}$$

7. With potassium chromate, K_2CrO_4:

$$(CH_3COO)_2Pb + K_2CrO_4 \longrightarrow \underset{\substack{\text{Lead chromate}\\ \text{(yellow ppt.)}}}{PbCrO_4\downarrow} + 2CH_3COOK$$

8. With HCl: On addition of HCl in $(CH_3COO)_2Pb$ solution, white ppt. of $PbCl_2$ is formed in cold conditions, which dissolves on heating. On cooling, $PbCl_2$ reappears as a white crystalline solid.

$$(CH_3COO)_2Pb + \underset{\text{dil}}{2HCl} \longrightarrow \underset{\substack{\text{Lead chloride}\\ \text{(white ppt.)}}}{PbCl_2} + 2CH_3COOH$$

9. With litharge: On boiling with litharge, basic lead acetate is formed.

$$(CH_3COO)_2Pb + PbO \longrightarrow \underset{\text{Basic lead acetate}}{Pb(OH)_2\cdot Pb(CH_3COO)_2}$$

Uses:

1. As a mordant in dyeing and calico printing.
2. In the manufacture of white lead.
3. In the manufacture of chrome yellow and chrome red, which are used as lead pigment.
4. In the qualitative analysis, for the detection of sulphide and chloride ions.
5. In medicine, for curing skin diseases.

7.15.21 Basic Lead Carbonate, $2PbCO_3\cdot Pb(OH)_2$

It is also known as white lead.

Preparation:

1. **Electrolytic process:** In this process, the electrolytic cell is divided into two chambers separated by a porous partition. The cathodes are made of sheet steal dipped in a solution of sodium carbonate. The anode chamber contains the anodes made of heavy lead plates dipped in sodium acetate solution. On passing electric current, the anodes are attacked by acetate ions and lead acetate is formed in the electrolyte. The solution of lead acetate reacts with Na_2CO_3 solution of the cathodic chamber, and white lead is formed.

$$CH_3COONa \rightleftharpoons \underset{\text{Anode}}{CH_3COO^{\ominus}} + Na^{\oplus}$$

$$\Big\downarrow \text{dissolves lead}$$

$$(CH_3COO)_2Pb$$

$$3Pb(CH_3COO)_2 + 4Na_2CO_3 + 2H_2O \longrightarrow 2PbCO_3\cdot Pb(OH)_2 + 2NaHCO_3 + 6CH_3COONa$$

White lead is washed with water and dried. Very fine uniform grains of white lead are obtained by this process.

Properties:

1. White amorphous powder.
2. Insoluble in water.
3. Posionous in nature.
4. On heating at 43°C, it decomposes to give red lead.

$$2PbCO_3\cdot Pb(OH)_2 \xrightarrow{43^\circ C} \underset{\text{Red lead}}{Pb_3O_4} + H_2O + CO_2 + CO$$

5. It is darkened in air, due to the formation of PbS.
6. It is soluble in linseed oil.

Uses:

1. White lead mixed with linseed oil is used as white paint.
2. It has large covering power.
3. It is generally mixed with $BaSO_4$, which increases its property of brushing out without affecting its covering power.

Drawback: The main drawback to the use of white lead are:

a. It becomes black if H_2S is present in atmosphere.
b. It is poisonous in nature.

ILLUSTRATION 7.6

a. Predict the products formed when Pb_3O_4 reacts with concentrated hydrochloric acid.
b. In which of the acid lead(II) oxide will dissolve: H_2SO_4 or HNO_3. Give reason.
c. Give the reaction between (i) HCl and PbO_2, (ii) SO_2 and PbO_2. Explain.

Sol.

a. Pb_3O_4 consists of $2PbO\cdot PbO_2$. Oxidation state of Pb in PbO_2 is +4; hence, PbO_2 will behave as an oxidising agent and will oxidise $HCl \rightarrow Cl_2$.

$$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + Cl_2 + 4H_2O$$

b. Lead(II) oxide reacts with H_2SO_4 to form lead(II) sulphate which is insoluble, whereas with HNO_3, it forms lead(II) nitrate which is soluble in water.

$$PbO + H_2SO_4 \longrightarrow \underset{\substack{\text{Lead sulphate}\\ \text{(white ppt.)}}}{PbSO_4\downarrow} + H_2O$$

$$PbO + 2HNO_3 \longrightarrow \underset{\substack{\text{Lead nitrate}\\ \text{(soluble)}}}{Pb(NO_3)_2} + H_2O$$

c. i. $\overset{(+4)}{PbO_2} + \overset{(-1)}{HCl} \longrightarrow \overset{(+2)}{PbCl_2} + H_2O + \overset{(0)}{Cl_2}$

In PbO_2, Pb is in +4 oxidation state, which being less stable than +2 oxidation state, gets reduced to +2 oxidation state. PbO_2 behaves as a strong oxidising agent and oxidises $HCl \longrightarrow Cl_2$.

ii. $\overset{(+4)}{PbO_2} + SO_2 \longrightarrow \overset{(+2)}{PbSO_4}$

In PbO_2, Pb is in +4 oxidation state, which is less stable +2 oxidation state. Thus, PbO_2 behave as a strong oxidising agent and oxidises SO_2 to SO_4^{2-}.

ILLUSTRATION 7.7

Give formula for the following:

a. Water glass
b. Phosgene
c. Litharge
d. Red lead
e. Butter of tin
f. Drykold
g. Chrome yellow
h. Carborundum
i. Sugar of lead
j. White lead

Sol.

a. Water glass, Na_2SiO_3
b. Phosgene, $COCl_2$
c. Litharge, PbO
d. Red lead, Pb_3O_4
e. Butter of tin, $SnCl_4 \cdot 5H_2O$
f. Drykold, dry CO_2 (CO_2 in solid state)
g. Chrome yellow, $PbCrO_4$
h. Carborundum, SiC
i. Sugar of lead, $Pb(CH_3COO)_2$
j. White lead, $2PbCO_3 \cdot Pb(OH)_2$

ILLUSTRATION 7.8

a. Which is more efficient fuel: water gas or producer gas?
b. The formula for mineral olivine $(Fe, Mg)_2SiO_4$ means that 2 mol of any combination of the metal ions is present per mol of orthosilicate ion. Does olivine follows the law of definite proportion? Is olivine a compound or a solid solution?

Sol.

a. Water gas is an equimolecular mixture of CO and H_2 in which both CO and H_2 burn and evolve heat, whereas producer gas is a mixture of CO and N_2 in which only CO burn and evolve heat. Thus, water gas is better or more efficient fuel than producer gas, since the calorific value of water gas will be more than that of producer gas.
b. Olivine, $(FeMg)_2SiO_4$, has any ratio of iron to magnesium and hence does not obey the law of definite proportion. It is therefore not a compound but a solid solution consisting of Fe_2SiO_4 in Mg_2SiO_4 or Mg_2SiO_4 in Fe_2SiO_4.

ILLUSTRATION 7.9

Indicate the principle ingredients of the following:

a. Coal gas
b. Producer gas
c. Water gas
d. Natural gas
e. Soft glass
f. Hard glass

Sol.

a. Coal gas: CH_4, CO, N_2, H_2
b. Producer gas: CO, N_2
c. Water gas: CO, H_2
d. Natural gas: CH_4, C_2H_6, C_3H_8
e. Soft glass: Na_2O, CaO, SiO_2
f. Hard glass: K_2O, CaO, SiO_2

ILLUSTRATION 7.10

Give reasons for the following:

a. Dil HCl is preferred as compared to dil H_2SO_4 for the preparation of CO_2 from marble.
b. CO_2 does not support combustion but a burning magnesium ribbon continues to burn in it.
c. PbO does not dissolve in H_2SO_4, while SnO is soluble.
d. NaOH cannot be stored in Sn or Pb vessel.
e. Alkanes are more stable than silanes.

Sol.

a. Marble, $CaCO_3$, reacts with dil H_2SO_4, to form white ppt. of $CaSO_4$, which gets deposited on the surface of the marble and acts as a protective layer. Thus, further reaction between marble and dil H_2SO_4 is prevented.

$$\underset{\text{dil}}{CaCO_3 + H_2SO_4} \longrightarrow \underset{\text{White ppt.}}{CaSO_4\downarrow} + CO_2\uparrow + H_2O$$

However, dil HCl reacts with marble to form $CaCl_2$, which does not get deposited on the marble surface and thus reaction between $CaCO_3$ and dil HCl resulting in the liberation of CO_2 continues.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2\uparrow + H_2O$$

b. CO_2 does not support combustion but burning magnesium ribbon continues to burn in it, as Mg reduces CO_2 to C and therefore Mg continues to burn in it.

$$CO_2 + 2Mg \longrightarrow C + 2MgO$$

c. PbO reacts with H_2SO_4 to form $PbSO_4$ which is insoluble in water and hence PbO does not dissolve in H_2SO_4.

$$PbO + H_2SO_4 \longrightarrow \underset{\substack{\text{Lead sulphate} \\ \text{(white ppt.)}}}{PbSO_4\downarrow} + H_2O$$

However, SnO on reaction with H_2SO_4 form $SnSO_4$, which is soluble; hence, SnO dissolves in H_2SO_4.

$$SnO + H_2SO_4 \longrightarrow SnSO_4 + H_2O$$

d. NaOH cannot be stored in Sn or Pb vessel as Sn and Pb dissolve in NaOH due to the formation of sodium stannate and sodium plumbate respectively, both of which are soluble.

$$Sn + 2NaOH + H_2O \longrightarrow \underset{\substack{\text{Sodium stannate} \\ \text{(soluble)}}}{Na_2SnO_2} + 2H_2$$

$$Pb + 2NaOH \longrightarrow \underset{\substack{\text{Sodium plumbate} \\ \text{(soluble)}}}{Na_2PbO_2} + H_2$$

e. Alkanes are more stable than silanes because C—C bonds in alkanes are more stable than Si—Si bonds in silanes due to greater extent of overlap between the $2sp^3$–$2sp^3$ hybridised orbitals of C as compared to $3sp^3$–$3sp^3$ hybridised orbitals of Si.

ILLUSTRATION 7.11

Give reasons:

a. CCl_4 is used as a fire extinguisher but not CS_2.

b. Sn is used to make solder.

c. The lead of lead pencil is not lead but graphite.

d. Despite the fact that carbon has only two unpaired electrons, it is tetravalent.

e. CCl_4 does not act as Lewis acid, while $SiCl_4$ does.

Sol.

a. CCl_4 is a heavy non-combustible liquid; hence, it can be used as fire extinguisher.

On the other hand, CS_2 is a highly combustible gas and cannot be used to extinguish fire.

$$2CS_2 + 5O_2 \longrightarrow 2CO + 4SO_2$$

b. Sn is easily fusible alloying metal and hence is used in making solder.

c. Graphite has got the property of marking paper whereas lead does not have this property. Hence, the lead in lead pencil is graphite and not lead.

d. Electronic configuration of carbon in the ground state is $2s^2\ 2p^2$, i.e. it has only two unpaired electrons. Despite this, carbon is always tetravalent, as the energy required for unpairing and promoting electron from $2s$ orbital to $2p$ orbital is more than compensated by the energy released when carbon forms four bonds, e.g. CX_4 type of compound. Hence, carbon is always tetravalent.

e. C in CCl_4 does not have vacant d-orbital in its valence shell in which it can accept an electron pair from other molecule/ion and hence CCl_4 has does act as Lewis acid, whereas Si in $SiCl_4$ has vacant $3d$-orbital in its valence shell and it can expand its coordination number from 4 to 6. Thus, $SiCl_4$ behaves as a Lewis acid.

ILLUSTRATION 7.12

A white coloured inorganic salt formed by an element of group 14 give the following reactions:

a. It is soluble in water and the solution has sweet taste.

b. The salt when heated gives acetone and a yellow coloured residue which is used in paints.

c. The solution of the salt gives a white precipitate with dil HCl which is soluble in hot water.

Explain the above observations with chemical reactions involved.

Sol. White coloured inorganic salt formed by an element of group 14 is lead acetate, $(CH_3COO)_2Pb$, which is commonly known as *sugar of lead*.

a. It is soluble in water and solution has sweet taste.

$$(CH_3COO)_2Pb + 2H_2O \longrightarrow 2CH_3COOH + Pb(OH)_2$$

b. Lead acetate on heating decomposes to give acetone and PbO, a yellow coloured residue which is used in paints.

$$(CH_3COO)_2Pb \xrightarrow{\text{Heat}} \underset{\substack{\text{Lead(II) oxide}\\\text{(Yellow residue)}}}{PbO\downarrow} + CO\uparrow + \underset{\text{Acetone}}{CH_3COCH_3}$$

c. When dil HCl is added to the solution of lead acetate, a white ppt. of $PbCl_2$ appears which is insoluble under cold conditions, but dissolves on heating.

$$(CH_3COO)_2Pb + 2HCl \longrightarrow \underset{\substack{\text{Lead chloride}\\\text{(white ppt.)}}}{PbCl_2\downarrow} + 2CH_3COOH$$

ILLUSTRATION 7.13

Give a balanced chemical reaction for the following:

a. Tin is heated with conc HNO_3.

b. Pb_3O_4 is treated with nitric acid.

c. Iodine is added to a solution of stannous chloride.

d. Dil HNO_3 is slowly reacted with metallic tin.

e. Passing $SiCl_4$ vapour over molten aluminium.

f. Stannous chloride is added to mercuric chloride.

g. Red lead is treated with conc H_2SO_4.

h. Red lead is treated with conc HCl.

Sol.

a. With conc HNO_3, hydrated stannic oxide (metastannic acid) (H_2SnO_3) is formed.

$$[NO_3^{\ominus} + 2H^{\oplus} + e^{\ominus} \longrightarrow NO_2 + H_2O] \times 4$$
$$Sn + 3H_2O \longrightarrow H_2SnO_3 + 4H^{\oplus} + 4e^{\ominus}$$
$$\overline{Sn + 4NO_3^{\ominus} + 4H^{\oplus} \longrightarrow H_2SnO_3 + 4NO_2 + H_2O}$$

b. Pb_3O_4 is a mixed oxide, $2PbO{\cdot}PbO_2$. With nitric acid, PbO is converted into $Pb(NO_3)_2$, whereas PbO_2 remains as such.

$$\underset{\substack{\text{or}\\(2PbO\cdot PbO_2)}}{Pb_3O_4} + 4HNO_3 \longrightarrow PbO_2 + \underset{\text{Lead nitrate}}{2Pb(NO_3)_2} + 2H_2O$$

c. Stannous chloride acts as a reducing agent and reduces $I_2 \rightarrow 2I^{\ominus}$ and itself gets oxidised to stannic chloride (Sn^{+4}).

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^{\ominus}$$
$$I_2 + 2e^{\ominus} \longrightarrow 2I^{\ominus}$$
$$\overline{Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^{\ominus}}$$

d. Tin reduces dil HNO_3 to ammonia (NH_3).

$$[Sn \longrightarrow Sn^{2+} + 2e^{\ominus}] \times 4$$
$$NO_3^{\ominus} + 10H^{\oplus} + 8e^{\ominus} \longrightarrow NH_4^{\oplus} + 3H_2O$$
$$\overline{4Sn + NO_3^{\ominus} + 10H^{\oplus} \longrightarrow 4Sn^{2+} + [NH_4]^{\oplus} + 3H_2O}$$

e. Crystalline silicon is prepared by passing $SiCl_4$ vapours over molten Al.

$$3SiCl_4 + 4Al \longrightarrow 4AlCl_3 + 3Si$$

Al being volatile passes over, while liberated Si dissolves in molten aluminium and separates as crystalline silicon.

f. $$\underset{\substack{\text{Stannous}\\\text{chloride}}}{SnCl_2} + \underset{\substack{\text{Mercuric}\\\text{chloride}}}{2HgCl_2} \longrightarrow \underset{\substack{\text{Stannic}\\\text{chloride}}}{SnCl_4} + \underset{\substack{\text{Mercurous}\\\text{chloride}}}{Hg_2Cl_2}$$

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^{\ominus}$$
$$2e^{\ominus} + 2Hg^{2+} \longrightarrow Hg_2^{2+}$$
$$\overline{Sn^{2+} + 2Hg^{2+} \longrightarrow Sn^{4+} + Hg_2^{2+}}$$

Stannous chloride acts as a reducing agent and reduces mercuric chloride to mercurous chloride and itself gets reduced to stannic chloride.

g. Red lead, Pb_3O_4, on reacting with conc H_2SO_4 liberates O_2 gas.

$$2Pb_3O_4 + 6H_2SO_4 \longrightarrow 6PbSO_4 + 6H_2O + O_2\uparrow$$

h. Red lead, Pb_3O_4, on reacting with conc HCl, oxidises $Cl^{\ominus}$ to Cl_2.

$$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2\uparrow$$

ILLUSTRATION 7.14

Give reasons for the following:

a. SnI_4 is orange in colour.
b. Solid ice is known as dry ice.
c. Diamond is inert, whereas graphite is not.
d. Nitrolim acts as a good nitrogenous fertiliser.

Sol.

a. SnI_4 absorbs blue light and reflects high proportion of orange or red. The energy absorbed in this way causes the transfer of an electron from I to Sn, which corresponds to the temporary oxidation of Sn(IV) to Sn(III). Since transferring an electron to another atom is same as transferring a charge, charge transfer complex is formed and due to which SnI_4 is orange in colour.

b. Solid ice at 1 atm pressure sublimes, i.e. changes from solid state to gaseous state, without liquefying. As a result, solid ice does not wet the surface and is known as dry ice.

c. In diamond, each C atom is sp^3 hybridised and a C-atom is tetrahedrally bonded to four other C-atoms, which means there is no unpaired electron left in the structure of diamond. Hence, it is inert, whereas in graphite, C is sp^2 hybrised and there is one unpaired electron on each C atom which is free and hence due to availability of unpaired electrons, graphite is reactive.

d. Nitrolim is CaNCN, i.e. calcium cyanamide. When added to the soil, it first changes into calcium carbonate and cyanamide.

$$CaNCN + H_2O + CO_2 \longrightarrow CaCO_3\downarrow + \underset{\text{Cyanamide}}{H_2N{\cdot}CN}$$

The cyanamide then hydrolyses into two steps:

i. $$H_2N{\cdot}CN + H_2O \longrightarrow \underset{\text{Urea}}{H_2NCONH_2}$$

ii. $$H_2NCONH_2 + H_2O \longrightarrow 2NH_3 + CO_2\uparrow$$

Ammonia (NH_3) is converted into nitrates by nitrifying bacteria. On account of its slow conversion into nitrates and NH_3, nitrolim or CaNCN acts as a good nitrogenous fertiliser.

CONCEPT APPLICATION EXERCISE 7.1

1. Why CCl_4 is resistant to hydrolysis, but $SiCl_4$ is readily hydrolysed?
2. No form of elemental silicon is comparable to graphite. Give reason.
3. Why carbon forms covalent compounds, whereas lead forms ionic compounds?
4. Give reason: Down the group (↓) tendency for catenation increases among group 14 elements.
5. Give one chemical reaction to show that tin(II) is a reducing agent whereas Pb(II) is not.
6. CO_2 is a gas, while SiO_2 is a high melting solid. Give reason.
7. Give one chemical reaction to explain why tin(II) chloride is a reducing agent.
8. C and Si are always tetravalent, but Ge, Sn and Pb show divalency. Give reason.
9. Tendency to exhibit +2 oxidation state increases with increasing atomic number among group 14 elements. Explain.
10. Why trimethylamine is pyramidal but trisilylamine is planar?
11. $(CH_3)_3N$ acts as a Lewis base, but $(SiH_3)_3N$ have very little basic character. Explain.
12. CO is stable, but analogous SiO is not stable. Why?
13. Why PbX_2 is more stable than PbX_4?
14. PbO_2 acts as a stronger oxidising agent than SnO_2. Comment.
15. Give reason: CO is readily absorbed by ammoniacal cuprous chloride, but not CO_2.
16. Silanes are few in number, whereas alkanes are large in number. Explain.
17. Are $(CH_3)_3N$ and $(SiH_3)_3N$ isostructural. Justify your answer.
18. For a mineral, $LiAl(SiO_3)_2$, what is the charge on SiO_3 unit? What is the arrangement of oxygen atoms around the silicon atom?
19. A metal M forms two chlorides MCl_2 and MCl_4, respectively. In which group, metal M can be placed?
20. An inorganic compound (X) made up of two most occurring elements in the earth's crust and used in building construction. When (X) reacts with carbon, it forms a poisonous gas (Y) which is most stable diatomic molecule. Identify compounds (X) and (Y).
21. Explain the following:
    a. Oil paintings turn blackish after sometime. What is the salt formed? Assume oil paints contain lead.

b. While testing oxalate ion, gas obtained burns with a blue flame initially but is put off instantly even as gas appears coming.

22. Complete the following:

a. $SnCl_2 + HCl + I_2 \longrightarrow (X) + (Y)$

b. Buckminsterfullerene or bucky ball is ________

c. When a mixture of air and steam is passed over red hot coke, the outgoing gas contains ________

Solved Examples

EXAMPLE 7.1

Identify (A) based on following facts:

a. (A) reduces $HgCl_2$ solution to white ppt. changing to grey.

b. (A) turns $FeCl_3$ yellow coloured solution to green.

c. (A) gives white ppt. with NaOH soluble in excess of NaOH.

d. (A) gives yellow dirty ppt. on passing H_2S gas, soluble in yellow ammonium sulphide (YAS).

e. (A) gives chromyl chloride test.

Sol. (A) gives yellow dirty ppt. soluble in YAS.

$\Rightarrow$ (A) has Sn^{2+}

(A) gives chromyl chloride test (of $Cl^{\ominus}$)

$\Rightarrow$ (A) has $Cl^{\ominus}$

$\Rightarrow$ (A) is $SnCl_2$

Explanation:

a. $SnCl_2 + 2HgCl_2 \longrightarrow \underset{\text{White ppt.}}{Hg_2Cl_2\downarrow} + SnCl_4$

$SnCl_2 + Hg_2Cl_2 \longrightarrow \underset{\text{Grey}}{2Hg} + SnCl_4$

b. $\underset{\text{Yellow}}{2FeCl_3} + SnCl_2 \longrightarrow \underset{\text{Green}}{2FeCl_2} + SnCl_4$

c. $SnCl_2 + 2NaOH \longrightarrow \underset{\text{White}}{Sn(OH)_2\downarrow} + 2NaCl$

$Sn(OH)_2 + 2NaOH \longrightarrow \underset{\substack{\text{Sodium stannate}\\ \text{(Soluble)}}}{Na_2SnO_2} + 2H_2O$

d. $SnCl_2 + H_2S \longrightarrow 2HCl + \underset{\text{Yellow}}{SnS\downarrow}$

$SnS + \underset{\text{(YAS)}}{(NH_4)_2S_2} \longrightarrow \underset{\text{Soluble}}{(NH_4)_2SnS_3}$

EXAMPLE 7.2

Oxalic acid on strong heating gives (A) and (B) which are gaseous product and (C) which is a liquid. Gas (A) burns with a blue flame and is oxidised to gas (B). Gas (B) turns lime water milky. Gas (A) on reaction with chlorine gas gives (D). (D) as well as (B) on heating with ammonia gas gives the same product, (E). Identify (A), (B), (C), (D) and (E).

Sol. Oxalic acid $\xrightarrow{\Delta} (A)_{(g)} + (B)_{(g)} + (C)_{(l)}$

Given, gas (A) burns with blue flame; hence, it must be carbon monoxide (CO).

Gas (A) gets oxidised to CO_2. Hence, (B) is carbon dioxide.

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{\Delta} \underset{(A)}{CO_{(g)}} + \underset{(B)}{CO_{2(g)}} + \underset{(C)}{H_2O_{(l)}}$$

(C) is water, H_2O.

Gas (B) turns lime-water milky due to the formation of calcium carbonate.

$$CO_2 + \underset{\text{Lime water}}{Ca(OH)_2} \longrightarrow \underset{\substack{\text{Calcium carbonate}\\ \text{(milkiness)}}}{CaCO_3\downarrow} + H_2O$$

Gas (A) on reaction with Cl_2 gives $COCl_2$, phosgene (D)

$$CO + Cl_{2(g)} \longrightarrow \underset{\text{Phosgene (D)}}{COCl_2}$$

Phosgene on heating with ammonia gives

$$\underset{(D)}{COCl_2} + 2NH_3 \longrightarrow \underset{\text{Urea (E)}}{H_2NCONH_2} + 2HCl$$

Carbon dioxide on heating with ammonia gives

$$\underset{(B)}{CO_2} + NH_3 \longrightarrow \underset{(E)}{H_2NCONH_2}$$

Hence, (A) is CO

(B) is CO_2

(C) is H_2O

(D) is $COCl_2$

(E) is H_2NCONH_2

EXAMPLE 7.3

An aqueous solution of salt (A) gives a white precipitate (B) with sodium chloride solution. Compound (B) dissolves in hot water and the solution on treatment with sodium iodide gives a yellow precipitate (D) and on passing H_2S through solution (B) gives a black ppt. (C). Compound (A) does not give any gas with dil HCl, but liberates a reddish brown gas on heating. Identify compounds (A), (B), (C) and (D).

Sol.

$$\text{Salt }(A)_{(aq)} + NaCl_{(aq)} \longrightarrow \underset{\text{white ppt.}}{(B)} + \text{filtrate}$$

Salt (A) $\xrightarrow{\Delta}$ Reddish brown gas

Salt (A) $\xrightarrow{\text{dil HCl}}$ No gas

(B) $\xrightarrow{\text{Hot water}}$ $(B)_{(aq)}$

$(B)_{(aq)} \xrightarrow{H_2S}$ Black ppt. (C)

$(B)_{(aq)} \xrightarrow{NaI}$ (D) Yellow ppt.

Salt (A) on heating liberates reddish brown gas; hence, it contains nitrate.

(B) dissolves in hot water and gives a yellow ppt. with NaI; hence, it is $PbCl_2$ and salt (A) is $Pb(NO_3)_2$.

$$\underset{(A)}{Pb(NO_3)_{2(aq)}} + 2\,NaCl_{(aq)} \longrightarrow \underset{\substack{\text{White ppt.}\\ (B)}}{PbCl_2\downarrow} + 2NaNO_{3(aq)}$$

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + \underset{\text{Reddish brown gas}}{2NO_2\uparrow} + 3O_2\uparrow$$

$$\underset{\substack{\text{White ppt.}\\ \text{(B)}}}{PbCl_2\downarrow} \xrightarrow{\text{Hot water}} Pb^{2+}_{(aq)} + 2Cl^{\ominus}_{(aq)}$$

$$PbCl_{2(aq)} + 2NaI \longrightarrow 2NaCl + \underset{\text{Yellow ppt. (D)}}{PbI_2\downarrow}$$

$$PbCl_{2(ag)} + H_2S \longrightarrow \underset{\text{Black ppt. (C)}}{PbS\downarrow} + 2HCl$$

Hence, (A) is $Pb(NO_3)_2$, lead nitrate

(B) is $PbCl_2$, lead chloride

(C) is PbS, lead sulphide

(D) is PbI_2, lead iodide.

EXAMPLE 7.4

Starting from $SiCl_4$ prepare the following in steps not exceeding the number given in parentheses (give reaction only)

a. Silicon (1)

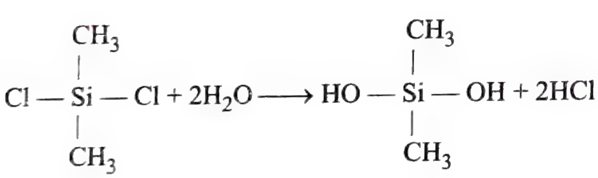
b. Linear silicon containing methyl groups only (4)

c. Na_2SiO_3 (3)

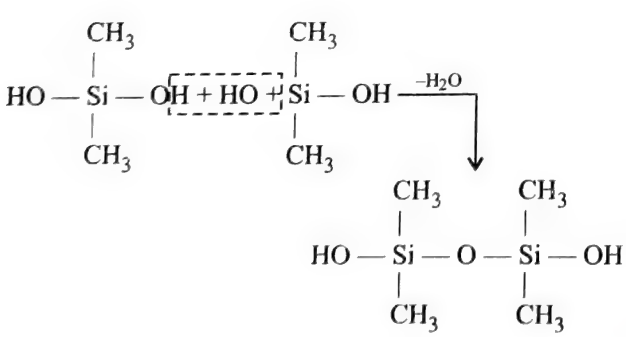
Sol.

a. $SiCl_4 + 2Mg \longrightarrow Si + 2MgCl_2$

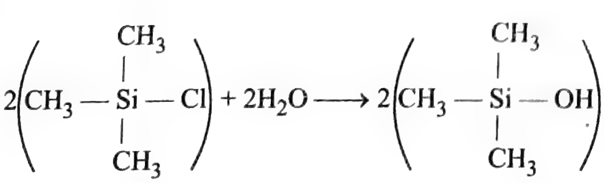
b. i.



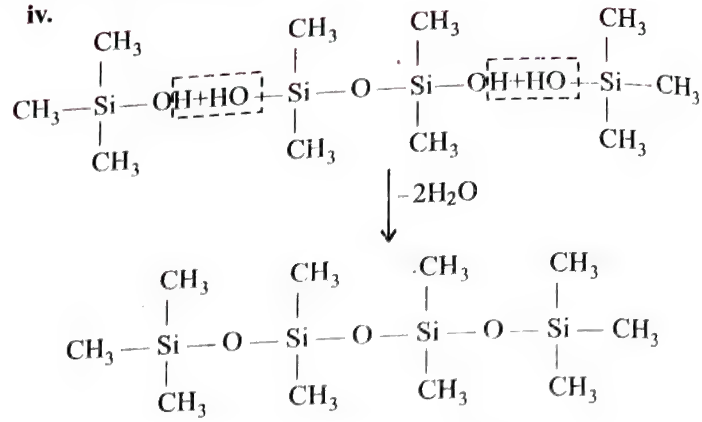
ii.



iii.



iv.



c. i. $SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$

ii. $Si(OH)_4 \xrightarrow{\text{Heat}} SiO_2 + 2H_2O$

iii. $SiO_2 + Na_2CO_3 \longrightarrow Na_2SiO_3 + CO_2\uparrow$

EXAMPLE 7.5

An element of group 14 form a red coloured mixed oxide (A), which on treatment with conc HNO_3 gives compound (B). (B) reacts with HCl to produce a chloride (C), which is insoluble in cold water but soluble in hot water. (A) on reaction with conc HCl produces (C). Identify (A), (B) and (C).

Sol. Lead (Pb) forms a red-coloured mixed oxide, known as red lead. Pb_3O_4 (A), which is a mixed oxide of PbO_2 and PbO in the ratio 1:2.

$$(A) + \underset{\text{Conc}}{HNO_3} \longrightarrow (B) \xrightarrow{HCl} (C)$$

(A) $\xrightarrow{\text{Conc HCl}}$ (C) Insoluble in cold water but soluble in hot water

$$\underset{(A)}{Pb_3O_4} + \underset{\text{conc}}{4HNO_3} \longrightarrow \underset{(B)}{2Pb(NO_3)_2} + PbO_2 + 2H_2O$$

$$\underset{(B)}{Pb(NO_3)_2} + 2HCl \longrightarrow \underset{\substack{(C)\\ \text{White ppt.}}}{PbCl_2\downarrow} + 2HNO_3$$

(C) $PbCl_2$, is insoluble in cold water but soluble in hot water.

$$\underset{(A)}{Pb_3O_4} + \underset{\text{Conc}}{8HCl} \longrightarrow \underset{(C)}{3PbCl_2} + 4H_2O + Cl_2$$

Pb_3O_4 acts as an oxidising agent and oxidises $2Cl^{\ominus} \rightarrow Cl_2$

Hence, (A) is Pb_3O_4, red lead

(B) is $Pb(NO_3)_2$, lead nitrate

(C) is $PbCl_2$, lead(II) chloride

EXAMPLE 7.6

$CaCO_3$ on heating gives a white solid (A) and a gas (B). (A) on heating with carbon gives a solid (C) and a gas (D). (C) on hydrolysis gives a gas (E) and a solid (F). Identify (A), (B), (C), (D), (E) and (F).

$$CaCO_{3(s)} \xrightarrow{\Delta} \underset{\text{White}}{(A)_{(s)}} + (B)_{(g)}$$

$$\downarrow \Delta \text{ Carbon}$$

$$(F) + (E)_{(g)} \xleftarrow{H_2O} (C)_{(s)} + (D)_{(g)}$$

$$CaCO_{3(s)} \xrightarrow{\Delta} \underset{(A)}{CaO_{(s)}} + \underset{(B)}{CO_2\uparrow_{(g)}}$$

$$CaO + 3C \longrightarrow \underset{(C)}{CaC_2} + \underset{(D)}{CO}$$

$$\underset{(C)}{CaC_2} + 2H_2O \longrightarrow \underset{(F)}{Ca(OH)_2} + \underset{(E)}{C_2H_2}$$

Hence (A) is calcium oxide, CaO.
(B) is carbon dioxide, CO_2.
(C) is calcium carbide, CaC_2.
(D) is carbon monoxide, CO.
(E) is acetylene, C_2H_2.
(F) is calcium hydroxide, $Ca(OH)_2$.

EXAMPLE 7.7

Choose the correct option:

a. A mixture of two gasses is formed when an organic acid is heated with conc H_2SO_4. When the gaseous mixture is passed through KOH solution, one gas is absorbed. The unabsorbed gas combines with chlorine and forms a poisonous gas. The organic acid and the two gases evolved with conc H_2SO_4 are, respectively:

i. CH_3COOH, CO_2, CO
ii. oxalic acid, CO_2, CO
iii. HCOOH, CO, H_2O
iv. None of these

b. $$2RCl + Si \xrightarrow[570\text{ K}]{\text{Cu powder}} R_2SiCl_2 \xrightarrow{H_2O} R_2Si(OH)_2 \xrightarrow{\text{Polymerisation}} (X)$$

(X) is

i. Cyclic silicon
ii. Cross-linked silicone
iii. Linear silicon
iv. None of these

c. Lead oxide (PbO) can be dissolved in

i. HNO_3
ii. HCl
iii. H_2SO_4
iv. H_2O

d. A colourless solution (A) gives black precipitate on passing H_2S. (A) also gives a white precipitate with stannous chloride which gradually changes to grey. Identify (A).

i. $PbCl_2$
ii. $CdBr_2$
iii. $HgCl_2$
iv. $Cu(NO_3)_2$

Sol.

a. Option (ii) is correct.

Oxalic acid on heating with H_2SO_4 gives a mixture of two gases: CO_2 and CO. H_2SO_4 acts as a dehydrating agent.

$$\underset{\text{Oxalic acid}}{\begin{matrix}COOH\\|\\COOH\end{matrix}} \xrightarrow[H_2SO_4]{\Delta} \underset{\text{Carbon dioxide}}{CO_2\uparrow} + \underset{\text{Carbon monoxide}}{CO\uparrow} + H_2O$$

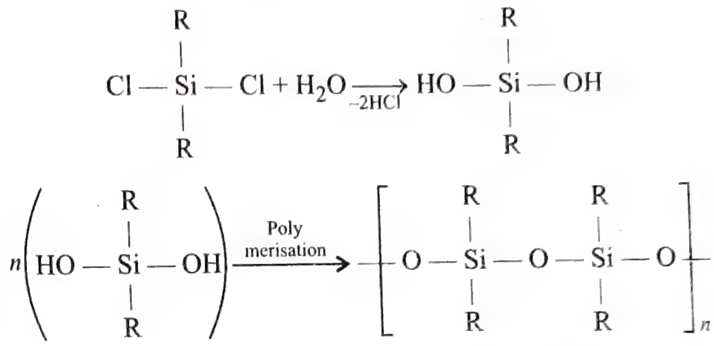
When this gaseous mixture, i.e. CO_2 and CO, is passed through KOH, CO_2 gets absorbed due to the formation of K_2CO_3, whereas CO remains as such.

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

CO combines with Cl_2 to form phosgene, $COCl_2$, a poisonous gas. Thus, the organic acid and the two gases evolved on heating with conc H_2SO_4 are oxalic acid, CO_2 and CO.

b. Option (iii) is correct.

$$2RCl + Si \xrightarrow[570\text{ K}]{\text{Cu powder}} R_2SiCl_2$$



Linear silicone

c. Option (i) is correct.

Lead oxide, PbO, dissolves in HNO_3 due to formation of lead nitrate, $Pb(NO_3)_2$, which is soluble.

$$PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$$

However, in HCl, H_2SO_4 and H_2O, it is insoluble.

$$PbO + 2HCl \longrightarrow \underset{\text{White ppt.}}{PbCl_2\downarrow} + H_2O$$

$$PbO + 2H_2SO_4 \longrightarrow \underset{\text{White ppt.}}{PbSO_4\downarrow} + 2H_2O$$

$$PbO + 2H_2O \longrightarrow \underset{\text{White ppt.}}{Pb(OH)_2\downarrow} + H_2O$$

d. Option (iii) is correct.

$$(A) \xrightarrow{H_2S\text{ gas}} \text{Black ppt.}$$

$$\downarrow SnCl_2$$

$$\text{White ppt.}$$

(A) The sulphide formed by passing H_2S gas is black; hence, it cannot be $CdBr_2$ as CdS is yellow.

$$Cd^{2+} + S^{2-} \longrightarrow \underset{\text{Yellow}}{CdS\downarrow}$$

(A) also reacts with $SnCl_2$ to give white ppt., which means (A) acts as on oxidising agent, oxidising $Sn^{2+} \longrightarrow Sn^{4+}$ and itself it is reduced.

$$HgCl_2 + H_2S \longrightarrow \underset{\text{Black ppt.}}{HgS\downarrow} + 2HCl$$

$$HgCl_2 + SnCl_2 \longrightarrow \underset{\text{White}}{Hg_2Cl_2} + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{\text{Grey}}{2Hg} + SnCl_4$$

EXAMPLE 7.8

Name the following compounds:

a. $(NH_4)_2CS_3$ b. $CaCS_3$
c. C_2N_2 d. $H_2C_3N_3O_3$
e. HCNS f. NH_2CSNH_2
g. $Fe(CNS)_3$ h. $CSCl_2$
i. Na_2CS_3 j. C_3O_2

k. O — COOH
|
H (H_2CO_3)

l. O — COOH
|
OH (H_2CO_4)

m. O — COOH
|
O — COOH $(H_2C_2O_6)$

n. $Na_2CO_3 \cdot H_2O$ 1/2 H_2O
o. $Na_2C_2O_6$ p. Na_2CO_4
q. $BaCO_4$

Sol.
a. Ammonium thiocarbonate
b. Calcium thiocarbonate
c. Cyanogen
d. Cyanuric acid
e. Thiocyanic acid
f. Thiourea
g. Ferric thiocyanate
h. Thio-carbonyl chloride
i. Sodium thiocarbonate
j. Carbon suboxide
k. Carbonic acid
l. Permono-carbonic acid
m. Perdicarbonic acid
n. Sodium carbonate perhydrate
o. Sodium per-di-carbonate
p. Sodium permono carbonate
q. Barium permono carbonate

EXAMPLE 7.9

$HgCl_2$ and $SnCl_2$ cannot exist together in an aqueous solution. Explain.

Sol. $SnCl_2$ is a strong reducing agent and hence reduces $HgCl_2$ first to Hg_2Cl_2 (white) and then to Hg (black). Hence, these do not exist together.

$$SnCl_2 + 2HgCl_2 \longrightarrow SnCl_4 + Hg_2Cl_2$$
$$SnCl_2 + Hg_2Cl_2 \longrightarrow SnCl_4 + Hg$$

EXAMPLE 7.10

The formula for two dimensional sheet silicate anion $(Si_xO_{y+z})^{3-}$ is calculate the value of $(x + z - y)$.

Sol. (12) Two dimensional sheet silicate has repeating units of $[Si_6O_{18}]^{12-}$

$\therefore\ x = 6, y + z = 18, z = 12$

$y = 18 - 12 = 6$

$\therefore\ (x + z - y) = (6 + 12 - 6) = 12$

EXAMPLE 7.11

Following silicates are given:

a. $ZnCa_2Si_2O_7$ b. $BaTi(Si_3O_9)$

If P = Total number of monovalent atoms in both silicates

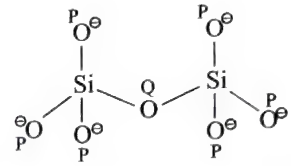
Q = Total number of bivalent atoms in both silicates

Calculate the value of P/Q

Sol. (3)

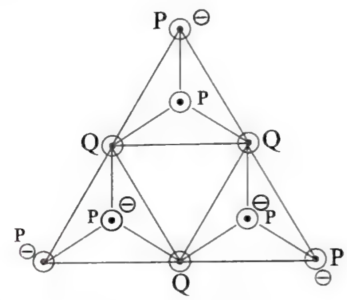
(a) $(Si_2O_7)^{6-}$ (Pyrosilicate) in which two tetrahedral share one O-atom.

$P = 6, Q = 1$



(b) $(Si_3O_9)^{6-}$ (cyclic or ring silicate) in which two O-atom per tetrahedra are shared.

$P = 6, Q = 3$



$\therefore P = 6 + 6 = 12, Q = 1 + 3 = 4$

$$\frac{P}{Q} = \frac{12}{4} = 3$$

EXAMPLE 7.12

Formula of tremolite asbestos is: $Ca_2Mg_x(Si_4O_{11})_2(OH)_2$.

Find the value of x.

Sol. (5)

If two chains are cross-linked, the resulting double stranded silicates have the composition $[(Si_4O_{11})^{6-}]_n$ and are called amphiboles. Asbestos belong to this class.

$$\overset{+2\times 2}{Ca_2}\ \overset{+2\times x}{Mg_x}\ \overset{-6\times 2}{(Si_4O_{11})_2}\ \overset{-1\times 2}{(OH)_2}$$

$\therefore\ 4 + 2x - 12 - 2 = 0$

$\therefore\ x = 5.$

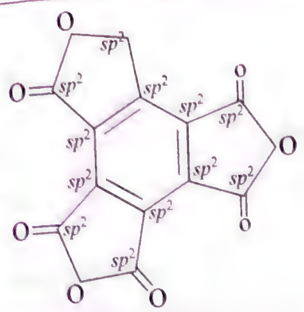
EXAMPLE 7.13

Consider the following four compounds.

a. C_xO_y b. C_xO_{y+1}
c. $C_{x+2}O_{y+1}$ d. $C_{x+11}O_{y+8}$

If $x = y = 1$, and P and Q are total number of sp and sp^2 hybridized C-atoms respectively. Then calculate the value of $\frac{P+Q}{5}$

(3.4)

Compound	Geometry	sp(c)	sp^2(c)
(a) CO	$:C\equiv O$ (Linear)	1	0
(b) CO_2	$O=C=O$ (Linear)	1	0
(c) C_3O_2	$O=C=C=C=O$ (Linear)	3	0
(d) $C_{12}O_9$		0	12
		5	12

$$\frac{P+Q}{5}=\frac{5+12}{5}=\frac{17}{5}=3.4$$

EXAMPLE 7.14

The formula of kinoite minerals is:

$Ca_2Cu_2^{+2}Si_3O_{10}.2H_2O$.

If x = Number of monovalent oxygen atom in the above compound

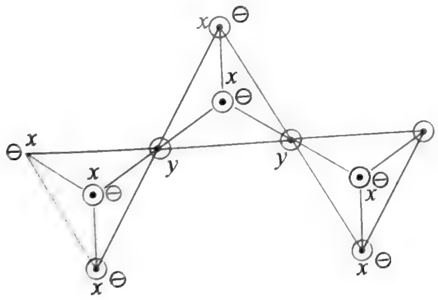
y = Number of divalent oxygen atom in the above compound.

Then, the value of $\frac{x-y}{3}$ is:

Sol. (2) The silicate anion $(Si_3O_{10})^{8-}$ in kinoite is a chain of three SiO_4^{-4} tetrahedra, that share corners with adjacent tetrahedra.

$\therefore\ x=8$

$y=2$



$$\frac{x-y}{3}=\frac{8-2}{3}=2$$

EXAMPLE 7.15

Identify A to K.

Three oxides of alkaline earth metals (A, B and C) on heating with C at 2000°C gives three compounds (D, E, F) and all of them give same gas (G).

Compound (D) on hydrolysis gives an alkane (H) while compound (E) gives an alkyne. Containing 3C(I) compound (F) on reaction with N_2 at 1100°C gives a nitrogenous fertilizer (I) which on hydrolysis give a gas (K) reacts with nessler's reagent.

Sol. Carbides of Be given CH_4 (Alkane). Carbides of Mg gives $CH_3C\equiv CH$ (Alkyne) nitrogenous fertilizer is $CaCN_2$. Thus A is BeO, B is MgO & C is CaO.

NH_3(g) reacts with Nessler's reagent , thus (K) is NH_3

Reaction:

(i) $\underset{(A)}{BeO}+3C\xrightarrow{2000°C}\underset{(D)}{Be_2C}+\underset{(G)}{CO\uparrow}$

$Be_2C\xrightarrow{4H_2O}\underset{(H)}{2CH_4\uparrow}+2Be(OH)_2$

(ii) $\underset{(B)}{2MgO}+5C\xrightarrow{2000°C}\underset{(E)}{Mg_2C_3}+\underset{(G)}{2CO\uparrow}$

$Mg_2C_3\xrightarrow{4H_2O}2Mg(OH)_2+\underset{(I)}{CH_3C\equiv CH}$

(iii) $\underset{(C)}{CaO}+3C\longrightarrow\underset{(F)}{CaC_2}+\underset{(G)}{CO\uparrow}$

$CaC_2\xrightarrow[1100°C]{N_2}\underset{(J)}{CaCN_2}+C\xrightarrow{3H_2O}CaCO_3+\underset{(K)}{2NH_3}$

(J) Calcium cyanamide (fertilizer)

Exercises

Single Correct Answer Type

Physical and chemical properties

1. In the carbon family, the elements other than carbon do not form $p\pi-p\pi$ bonds because the atomic orbitals are:
   (1) Small and diffuse to undergo effective lateral overlap.
   (2) Large and diffuse to undergo effective lateral overlap.
   (3) Large and far too less diffuse to overlap linearly.
   (4) Small to overlap both laterally and linearly.
2. Interlayer distance in graphite is:
   (1) Very small, the layers being tightly packed
   (2) Many times larger than the covalent radius of carbon
   (3) More than twice the covalent radius of carbon
   (4) The same as the covalent radius of carbon
3. Carbon forms a large number of compounds due to:
   (1) Tetravalency (2) Variable valency
   (3) Large chemical affinity (4) Property of catenation
4. The hybrid states of C in diamond and graphite are respectively:
   (1) sp^2, sp^3 (2) sp^3, sp^2
   (3) sp^2, sp^2 (4) sp^3, sp^3
5. Which of the following statement is false about carbon?
   (1) C_{60} is also one of the allotrope of carbon
   (2) It has crystalline as well as amorphous allotropes
   (3) It can form $p\pi-p\pi$ bond with other C-atoms.
   (4) It cannot form $p\pi-p\pi$ bond with atoms such as N and O
6. The use of diamond as a gem depends on its
   (1) hardness (2) high refractive index
   (3) purest form of carbon (4) chemical inertness
7. Which of the following is chemically inactive allotropic form of carbon?
   (1) Coal (2) Diamond
   (3) Charcoal (4) Animal charcoal
8. In CH_4, valency of carbon is four. Valency of carbon in acetylene is
   (1) 1 (2) 2
   (3) 3 (4) 4
9. Which of the following is a good conductor of electricity?
   (1) Diamond (2) Graphite
   (3) Coal (4) None of these
10. Carbon shows tetravalency due to
    (1) sp^3 hybridisation (2) dsp^2 hybridisation
    (3) sp^2 hybridisation (4) All of these
11. The element which forms only one hydride is:
    (1) C (2) Si
    (3) Ge (4) Pb
12. In the ground state, carbon atom has how many unpaired electron(s)?
    (1) 1 (2) 2
    (3) 3 (4) 4
13. Which of the following has least tendency to undergo catenation?
    (1) C (2) Si
    (3) Ge (4) Sn
14. Which of the following statement is not correct?
    (1) Silicon is extensively used as a semiconductor.
    (2) Carborundum is SiC.
    (3) Silicon occurs in free state in nature.
    (4) Mica contains the element silica.
15. Lead dissolves most readily in
    (1) acetic acid (2) sulphuric acid
    (3) nitric acid (4) hydrochloric acid
16. Which of the following metals is an important ingredient of transistors?
    (1) Osmium (2) Germanium
    (3) Gold (4) Sodium
17. The material used in solar cells contains:
    (1) Si (2) Sn
    (3) Ti (4) Cs
18. 'Softening of lead' means:
    (1) Conversion of lead to PbO.
    (2) Conversion of lead to Pb_3O_4.
    (3) Removal of impurities (metallic) from lead.
    (4) Washing lead with HNO_3 followed by a dilute alkali solution.
19. Graphite is soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite
    (1) has carbon atoms arranged in large planes of rings of strongly bound carbon atoms with weak interplanar bonds
    (2) is a non-crystalline substance
    (3) is an allotropic form of carbon
    (4) has molecules of variable molecular masses like polymers
20. Beryllium and aluminium carbides contain
    (1) C^{4-} (2) C_2^{2-}
    (3) C_3^{2-} (4) C^{4+}
21. Which of the following halide of carbon is used as refrigerant?
    (1) CCl_4 (2) CF_4
    (3) CH_2Cl_2 (4) CCl_2F_2
22. Which of the following statements is not correct?
    (1) Lead salts are slow poisons.
    (2) Lead metal is used in accumulators.
    (3) Plumbosolvency increases by the presence of carbonates, sulphates, phosphates etc.
    (4) Lead is a soft metal.

23. C_{60} contains
(1) 20 pentagons and 12 hexagons
(2) 12 pentagons and 20 hexagons
(3) 30 pentagons and 30 hexagons
(4) 24 pentagons and 36 hexagons

24. C_{60} can be regarded as a huge ball made up of:
(1) Several conjugated alkene units rather than an aromatic molecule.
(2) Graphite units.
(3) Several aromatic benzene molecules.
(4) Several tetrahedrons.

25. Often a ground glass stopper gets stuck in the neck of a glass bottle containing NaOH solution. This is due to:
(1) The presence of dirt particles in between.
(2) The formation of solid silicate in-between by the reaction of SiO_2 of glass with NaOH.
(3) The formation of Na_2CO_3 in-between by the reaction of CO_2 of air and NaOH.
(4) Glass contains a boron compound which forms a precipitate with the NaOH solution.

26. C–C bond length is maximum in
(1) diamond (2) graphite
(3) naphthalene (4) fullerene

27. When a lead salt is heated with sodium carbonate in charcoal cavity, it gives
(1) yellow incrustation (2) brown
(3) black (4) blue

28. Lead solution may be titrated with standard EDTA at pH = 6 using which indicator?
(1) Methyl thymol blue (2) Eriochrome Black T
(3) Methyl orange (4) Eosin

29. For making good quality mirrors, plates of float glass are used. These are obtained by floating molten glass over in liquid metal, which does not solidify before the glass. The metal used is
(1) Hg (2) Sn
(3) Na (4) Mg

30. The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence:
(1) $PbX_2 < SnX_2 < GeX_2 < SiX_2$
(2) $GeX_2 < SiX_2 < SnX_2 < PbX_2$
(3) $SiX_2 < GeX_2 < PbX_2 < SnX_2$
(4) $SiX_2 < GeX_2 < SnX_2 < PbX_2$

31. Which is likely to show inert pair effect?
(1) K (2) Mg
(3) Al (4) Pb

32. Which of the following oxidation states are most characteristic for lead and tin, respectively?
(1) +2, +4 (2) +4, +4
(3) +2, +2 (4) +4, +2

33. Among the following the INCORRECT statement is:
(1) Diamond and graphite are two allotropes of carbon.
(2) In diamond each C is sp^3 hybridised.
(3) In graphite each C is sp^2 hybridised.
(4) Graphite shows high electrical conductivity in one direction only.

34. Silicon shows diagonal relationship with
(1) Al (2) Be
(3) B (4) Mg

35. Select incorrect statement
(1) Graphite conducts electricity due to highly delocalized nature of π-electrons
(2) Graphite has planar hexagonal layers of C-atoms held together by weak van der Waals forces
(3) Thermodynamically most stable allotropes of carbon
(4) C—C bond length is higher as compared to diamond

36. Select incorrect statement
(1) Stability of hydrides of 14 group elements is: $CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$
(2) The tendency for catenation of 14 group elements is: $C >>> Si > Ge = Sn >>> Pb$
(3) During freezing winter, Sn is converted to grey powder due to the formation SnO_2
(4) When Cl_2 is passed through molten Sn, $SnCl_4$ is formed

37. Select incorrect statement
(1) Water gas is a mixture of $(CO + H_2)$
(2) Producer gas is a mixture of $(CO + N_2)$
(3) LPG is a mixture of *n*-butane and isobutene
(4) Bio gas is ethylene

38. Select correct statement
(1) Lead pencil contains 95% of Pb
(2) Si do not form $p\pi$-$p\pi$ multiple bond due to large and less diffuse atomic orbitals
(3) Graphite on heating with conc. HNO_3, gives a yellow mass called graphite nitrate
(4) Carbon, a mixture of 90% O_2 and 10% CO_2 is used for artificial respiration.

39. Select correct statement
(1) Al reacts with dil. H_2SO_4 to give H_2 gas
(2) Tincal is a mineral of boron.
(3) CO is combustible and CO_2 is non-combustible
(4) Quartz, tridymite and agate are the three crystalline forms of silica.

40. Select incorrect statement
(1) Sn gives sulphates and nitrates but Si does not
(2) CO is poisonous because it deoxygenates blood
(3) One carat = 200 mg
(4) Buckminster fullerene is an allotrope of Sn

Compounds of 14 group

41. Which of the following statement is false about CO_2 ?
(1) It has linear structure
(2) It has same number of sigma and pi bonds
(3) Its molecule contains two π-electrons.
(4) It turns lime water milky.

42. Which oxide of carbon is useful in preparing metal carbonyls?
(1) CO_2 and CO
(2) CO
(3) CO_2
(4) CO_2 and C_3O_2

43. Producer gas is a mixture of:
(1) $CO + N_2$
(2) $N_2 + H_2$
(3) $CO + H_2$
(4) $CO_2 + H_2O$

44. Which statement is not true about CO?
(1) It is a colourless gas.
(2) It is an odourless gas.
(3) It is highly soluble in water.
(4) It is a poisonous gas.

45. Which of the following is a covalent carbide?
(1) CaC_2
(2) Al_4C_3
(3) WC
(4) SiC

46. Which of the following is known as pyrene?
(1) CS_2
(2) Al_4C_3
(3) CCl_4
(4) Solid CO_2

47. Which of the following oxide will produce hydrogen peroxide on treatment with water?
(1) $KClO_3$
(2) Na_2O_2
(3) CaO
(4) SO_3

48. Five extinguishers contain a bottle of H_2SO_4 and
(1) $CaCO_3$
(2) $MgCO_3$
(3) $NaHCO_3$
(4) Any carbonate

49. A colourless gas which burns with blue flame and reduces CuO to Cu is:
(1) N_2
(2) CO
(3) CO_2
(4) NO_2

50. The species present in solution when CO_2 is dissolved in water are:
(1) H_2CO_3, CO_3^{2-}
(2) $HCO_3^{\ominus}$, CO_3^{2-}
(3) CO_2, H_2CO_3
(4) CO_2, H_2CO_3, $HCO_3^{\ominus}$, CO_3^{2-}

51. A when added to silica gives B. A and B are:
(1) HF, H_2SiF_4
(2) HF, H_2SiF_6
(3) HCl, H_2SiCl_6
(4) HI, H_2SiI_6

52. Among the following substituted silanes, the one which will give rise to cross-linked silicone polymer on hydrolysis is:
(1) R_3SiCl
(2) R_4Si
(3) $RSiCl_3$
(4) R_2SiCl_2

53. The correct order of increasing C—O bond length of CO, CO_2 and CO_3^{2-} is:
(1) $CO_3^{2-} < CO_2 < CO$
(2) $CO_2 < CO_3^{2-} < CO$
(3) $CO < CO_3^{2-} < CO_2$
(4) $CO < CO_2 < CO_3^{2-}$

54. On heating $Pb(NO_3)_2$, the products formed are:
(1) PbO, N_2, O_2
(2) $Pb(NO_2)_2$, O_2
(3) PbO, NO_2, O_2
(4) Pb, N_2, O_2

55. The product of the following reaction are:

$$SiO_2 + C \xrightarrow{\Delta} \text{Products}$$

(1) SiC and CO_2
(2) SiO and CO
(3) SiC and CO
(4) Si and CO

56. In silicon dioxide:
(1) There are double bonds between silicon and oxygen atoms.
(2) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms.
(3) Silicon is bonded to two silicon atoms.
(4) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms.

57. In the manufacture of glass, the addition of MnO_2 gives:
(1) Yellow colour
(2) Red colour
(3) Violet colour
(4) Pink colour

58. Solder is an alloy of:
(1) 70% Pb, 30% Sn
(2) 33% Pb, 67% Sn
(3) 80% Pb, 20% Sn
(4) 90% Cu, 10% Sn

59. Solid carbon dioxide is used as:
(1) Poison
(2) Fire extinguisher
(3) Refrigerant
(4) Artitificial respiration

60. When PbO_2 reacts with conc HNO_3, the gas evolved is:
(1) NO_2
(2) O_2
(3) N_2
(4) N_2O

61. When steam reacts with red hot coke to form CO_2 and hydrogen:
(1) Water acts as an oxidising agent.
(2) Water acts as a reducing agent.
(3) Carbon acts as an oxidising agent.
(4) There is no oxidation or reduction.

62. CCl_4 is used as fire extinguisher because:
(1) It has high melting point.
(2) It forms covalent bond.
(3) Its boiling point is low.
(4) It gives combustible vapours.

63. The most unstable compounds of the following are:
(1) hydrides of C
(2) hydrides of Sn
(3) hydrides of Ge
(4) hydrides of Pb

64. Which of the following is most basic?
(1) CO
(2) GeO
(3) SnO
(4) PbO

65. Bond energy is highest for:
(1) Sn—Sn
(2) C—C
(3) Si—Si
(4) Ge—Ge

66. What is the formula of carbon suboxide?
(1) CO
(2) CO_2
(3) C_2O_4
(4) C_3O_2

67. CO is absorbed by:
(1) Alcohols
(2) Plants
(3) An ammonical solution of cuprous chloride
(4) Nickel tetracarbonyl

68. Carbogen is given to pneumonia patients and victims of CO poisoning as a:
(1) Mixture of oxygen with 5–10% CO_2
(2) Mixture of helium with 5–10% CO_2
(3) Mixture of oxygen with 20–30% CO_2
(4) Mixture of helium with 20–30% CO_2

69. $[SiO_4]^{4-}$ has a tetrahedral structure. The silicate formed by using three oxygen has a:
(1) Linear polymeric structure
(2) Three-dimensional structure
(3) Pyrosilicate structure
(4) Two-dimensional sheet structure

70. The structure and hybridisation of $Si(CH_3)_4$ is:
(1) Bent, sp
(2) Trigonal, sp^2
(3) Octahedral, sp^3d^2
(4) Tetrahedral, sp^3

71. Structural units of ice and dry ice are, respectively.
(1) H_2O, CO
(2) H_2O, CO_2
(3) CO_2, H_2O
(4) CO, CO_2

72. A fuel will have a large fuel value when one gram of it on heating gives more of
(1) CO_2
(2) Ash
(3) Water vapours
(4) Calories

73. Which of the following oxides has a three-dimensional structure?
(1) CO
(2) CO_2
(3) SiO_2
(4) SO_2

74. CCl_4 is inert towards hydrolysis but $SiCl_4$ is readily hydrolysed because:
(1) Carbon cannot expand its octet but silicon can expand its octet.
(2) Ionisation enthalpy of carbon is higher than silicon.
(3) Electronegativity of carbon is higher than that of silicon.
(4) Carbon forms double and triple bonds.

75. The number and type of bonds between two carbon atoms in CaC_2 are:
(1) One sigma and one pi bond.
(2) One sigma and two pi bonds.
(3) One sigma and one half pi bond.
(4) One sigma bond.

76. The anhydride of carbonic acid is:
(1) CO
(2) CO_2
(3) C_3O_2
(4) none of these

77. Me_2SiCl_2 on hydrolysis will produce:
(1) $Me_2Si(OH)_2$
(2) $Me_2Si=O$
(3) $\lbrack O-(Me)_2Si-O \rbrack_n$
(4) $Me_2SiClOH$

78. Silica is reacted with sodium carbonate. What is the gas liberated?
(1) CO
(2) O_2
(3) CO_2
(4) O_3

79. The straight chain polymer is formed by:
(1) Hydrolysis of CH_3SiCl_3 followed by condensation polymerisation.
(2) Hydrolysis of $(CH_3)_4Si$ followed by addition polymerisation.
(3) Hydrolysis of $(CH_3)_2SiCl_2$ followed by condensation polymerisation.
(4) Hydrolysis of $(CH_3)_3SiCl$ followed by condensation polymerisation.

80. $K_2C_2O_6$ is called
(1) Potassium per carbonate
(2) Potassium permono carbonate
(3) Potassium perdicarbonate
(4) Potassium subcarbonate

81. Carbon suboxide C_3O_2 ($O=C=C=C=O$) is obtained as a colourless gas by the dehydration of malonic acid with
(1) Conc H_2SO_4
(2) H_3PO_4
(3) P_4O_{10}
(4) All

82. Which of the following is a true acid anhydride?
(1) Al_2O_3
(2) CO
(3) CO_2
(4) CaO

83. Which of the following anions are present in clay?
(1) $(Si_2O_5^{2-})_n$
(2) $(Si_4O_{11}^{6-})_n$
(3) $(SiO_3^{2-})_n$
(4) (SiO_4^{4-})

84. Double chain structures are present in asbestos. Which of the anions are present in them?
(1) $(Si_2O_5^{2-})_n$
(2) $(Si_4O_{11}^{6-})_n$
(3) $(SiO_3^{2-})_n$
(4) (SiO_4^{4-})

85. Different forms of silica such as quartz, tridymite and cristobalite are as follows:

$$\underset{(SiO_2)}{\text{Quartz}} \xrightarrow{870^\circ C} \underset{(SiO_2)}{\text{Tridymite}} \underset{}{\overset{1470^\circ C}{\rightleftharpoons}} \underset{(SiO_2)}{\text{Cristobalite}}$$

The structure possessed in them is:
(1) Sheet silicate
(2) Three-dimensional silicate
(3) Chain silicate
(4) Cyclic or ring silicate

86. Pyro-silicates are formed by
(1) SiO_4^{4-} tetrahedra
(2) $(Si_2O_7^{6-})$
(3) $(SiO_3^{2-})_n$
(4) $(Si_2O_5^{12-})_n$

87. The plague or tin pest or tin disease refers to
(1) Conversion of Sn^{2+} salts to Sn^{4+} salts
(2) Conversion of white tin to grey tin
(3) Conversion of grey tin to white tin
(4) Emission of sound while bending a tin

88. The substance used as a smoke screen in warfare is
(1) $SiCl_4$
(2) $SnCl_4$
(3) $PbCl_4$
(4) $GeCl_4$

89. Carbonyl chloride (phosgene, $COCl_2$) is prepared by
(1) the combination of CO with Cl_2 in sunlight
(2) the action of 80% fuming H_2SO_4 boiling in CCl_4
(3) oxidising $CHCl_3$ with $K_2Cr_2O_7$ and H_2SO_4
(4) all of the above

90. Fusible alloys of lead with Bi and Sn are used for making soft solder, electric fuses, safety plug for boilers and automatic water sprinkles to prevent fire. They melt at low temperature.
(1) Wood's metal (2) Lipowitz alloy
(3) Rose's metal (4) All of the above

91. Which of the following reaction does not take place?
(1) $2HgCl_2 + Sn^{2+} \rightarrow Hg_2Cl_2 + Sn^{4+} + 2Cl^{\ominus}$
(2) $2Fe^{3+} + Sn^{2+} \rightarrow Sn^{4+} + 2Fe^{2+}$
(3) $2Fe^{2+} + Sn^{2+} \rightarrow 2Fe^{3+} + Sn$
(4) $Hg_2Cl_2 + Sn^{2+} \rightarrow 2Hg + Sn^{4+} + 2Cl^{\ominus}$

92. Island structure is possessed by
(1) orthosilicate (2) pyro-silicate
(3) chain silicate (4) sheet silicate

93. Which of the following structure is similar to graphite?
(1) B_4C (2) B_2H_6
(3) BN (4) B

94. Which of these is not a monomer for a high molecular mass silicone polymer?
(1) Me_3SiCl (2) $PhSiCl_3$
(3) $MeSiCl_3$ (4) Me_2SiCl_2

95. The basic structural unit of silicates is:
(1) SiO_3^{2-} (2) SiO_4^{2-}
(3) $SiO^{\ominus}$ (4) SiO_4^{4-}

96. $SiCl_4 \xrightarrow{H_2O} (X) \xrightarrow{1000°C} (Y)$
In the above reaction, (X) and (Y), respectively are:
(1) SiO_2 and Si (2) H_4SiO_4 and SiO_2
(3) H_2SiCl_6 and SiO_2 (4) H_4SiO_4 and Si

97. Al_4C_3 on hydrolysis gives
(1) CH_4 (2) C_2H_6
(3) C_2H_4 (4) C_2H_2

98. In SiF_6^{2-} and $SiCl_6^{2-}$, which one is known and why?
(1) SiF_6^{2-} because of the small size of F.
(2) SiF_6^{2-} because of the large size of F.
(3) $SiCl_6^{2-}$ because of the small size of Cl.
(4) $SiCl_6^{2-}$ because of the large size of Cl.

99. PbF_4 and $PbCl_4$ exists, but $PbBr_4$ and PbI_4 do not exist because of
(1) large size of $Br^{\ominus}$ and $I^{\ominus}$
(2) strong oxidising character of Pb^{4+}
(3) strong reducing character of Pb^{4+}
(4) low electronegativity of $Br^{\ominus}$ and $I^{\ominus}$

100. Biogas and producer gas are made up of:
(1) biogas contains CO_2 but producer gas does not.
(2) producer gas contains CO but not CO_2.
(3) both biogas and producer gas have N_2.
(4) all are correct.

101. The hybrid state of carbon atoms in C_{60} molecule is:
(1) *sp* (2) sp^2
(3) sp^3 (4) dsp^2

102. Hydrolysis of $(CH_3)_2SiCl_2$ and CH_3SiCl_3 leads to
(1) Linear chain and cross-linked silicones respectively.
(2) Cross-linked and linear chain silicones respectively.
(3) Linear chain silicones only.
(4) Cross-linked silicones only.

103. Egyptian blue ($CaCuSi_4O_{10}$) is an example of
(1) Sheet silicates (2) Cyclic silicates
(3) Pyrosilicates (4) Chain silicates

104. The average value of C–C bond order in graphite is:
(1) 4/3 (2) 3/4
(3) 3/2 (4) 1

105. Brilliance of diamond is due to
(1) Shape (2) Cutting
(3) Reflection (4) Total internal reflection

106. The silicate anion in the mineral kinoite is a chain of three SiO_4^{4-} tetrahedra, that share corners with adjacent tetrahedra. If the oxidation state of Si and O-atom in the silicate anion in kinoite respectively are x and y then $x + y$ is:
(1) –2 (2) –4
(3) –6 (4) –8

107. Select the incorrect statement
(1) $(Si_2O_5)_n^{2n-}$ anion is obtained when 3 O-atom of SiO_4^{4-} tetrahedra are shared with another SiO_4^{4-} tetradedron
(2) Silicates having one monovalent corner O-atom in each tetrahedron unit is sheet silicate
(3) In cyclic silicate only two corners per tetrahedron are shared
(4) In single chain silicate 3 corners per tetrahedron are shared

108. Select incorrect statement
(1) In amphibole silicate structure 2 corner per tetrahedron are shared. Average shared corner is 2.5
(2) In pyro-silicate one corner O-atom/T.H. is shared. Each Si atom is surrounded by 3.5 O-atom
(3) In double chain silicates 3 corner per/T.H. is shared
(4) The anion of silicate, $Si_6O_{18}^{12-}$ represents cyclic silicate

109. The silicate anion is the mineral kinoite is a chain of three SiO_4^{4-} tetrahedra that share corners with adjacent tetrahedra. The mineral also contains Ca^{2+}, Cu^{2+} ions, and H_2O molecules in a 1:1:1 ratio, mineral is represented by.
(1) $CaCuSi_3O_{10}.2H_2O$ (2) $Ca_2Cu_2Si_3O_{10}.2H_2O$
(3) $CaCuSi_3O_{10}.H_2O$ (4) None of these

110. Select incorrect statement
(1) PbO is most basic in 14 group elements
(2) Sn^{4+} is more stable than Pb^{4+}
(3) Pb^{+2} is more stable than Sn^{2+}
(4) Tl^{+3} is more stable than Tl^{+1}

111. Select the incorrect statement
(1) Carbon suboxides is obtained on dehydration of malonic acid with P_4O_{10}
(2) PbI_4 does not exist because Pb^{+4} is oxidizing and $I^{\ominus}$ is strong reducing agent

(3) Structural feature of SiO_2 is macro-molecular with a non-layer structure

(4) $SiCl_4$ on hydrolysis gives silicone.

Multiple Correct Answers Type

Physical and chemical properties

1. Carbon differs from the rest of the family members because of:
   (1) Number of unpaired electrons in valence shell
   (2) Small size
   (3) Non-availability of vacant orbitals in valence shell
   (4) Non-availability of *d*-orbitals in valence shell

2. Which among the following statements are correct?
   (1) Aquadag and oildag are made up of graphite
   (2) Graphite reacts with conc HNO_3 to form mellitic acid $C_6(COOH)_6$
   (3) Both CO and C_3O_2 are toxic.
   (4) Zircon ($ZrSiO_4$) is a gemstone.

3. Which of the following are the ores of lead?
   (1) Galena (2) Cassiterite
   (3) Anglesite (4) Cerussite

4. In its compounds, tin exhibits the oxidation numbers
   (1) + 2 (2) + 4
   (3) + 6 (4) + 3

5. Which is/are likely to show inert pair effect?
   (1) K (2) Mg
   (3) Ga (4) Pb

6. With respect to diamond and graphite, which of the statement(s) given below is/are corrects?
   (1) Graphite is harder than diamond.
   (2) Graphite has higher electrical conductivity than diamond.
   (3) Graphite has higher thermal conductivity than diamond.
   (4) Graphite has higher C–C bond order than diamond.

7. Select the correct statement about fullerenes (C_{60})
   (1) C_{60} structure has 12 five membered and 20 six membered rings.
   (2) Six membered rings are fused to other six membered as well as to five membered rings.
   (3) Five membered rings are fused to only six membered rings.
   (4) There are alternate single and double bond and each atom is sp^2-hybridised with extensive delocalized molecular orbital

8. Select the correct statements about fullerenes (C_{70})
   (1) It has 12 five membered and 25 six membered rings.
   (2) Six membered and five membered rings are fused in same manner as in C_{60}
   (3) Buck minster fuller was a chemist
   (4) Kroto, smalley and curl got the noble prize in chemistry in 1996 for the discovery of fullerenes

9. Select incorrect statement
   (1) Sn on reaction with dil. HNO_3, gives $Sn(NO_3)_2$ and $NO_2(g)$
   (2) Pb on reaction with con. HNO_3, gives $Pb(NO_3)_2$ and $NO(g)$
   (3) Sn on reaction with conc. HNO_3 gives $Sn(NO_3)_2$ and $NO_2(g)$
   (4) Purple of casius is obtained when $SnCl_2$ reacts with $AuCl_3$

Compounds of 14 groups

10. Compounds which readily undergo hydrolysis are:
    (1) CCl_4 (2) BCl_3
    (3) $SiCl_4$ (4) CF_4

11. The non-existence of PbI_4 is due to
    (1) highly oxidising nature of Pb^{4+}
    (2) highly reducing nature of Pb^{4+}
    (3) sufficiently large covalent character
    (4) highly reducing nature of $I^{\ominus}$ ions

12. Which are not correct?
    (1) $Ge(OH)_2$ is amphoteric
    (2) $SnCl_4$ is more stable than $SnCl_2$
    (3) Trisilylamine is pyramidal
    (4) $GeCl_4$ in HCl forms $H_2[GeCl_6]$

13. Which of the following carbides on treatment with water give methane?
    (1) CaC_2 (2) Be_2C
    (3) Al_4C_3 (4) Mg_2C_3

14. Carbon dioxide is isostructural with
    (1) $HgCl_2$ (2) $SnCl_2$
    (3) C_2H_2 (4) NO_2

15. CO is isostructural with:
    (1) $SnCl_2$ (2) $HgCl_2$
    (3) SCl_2 (4) ZnI_2

16. Which of the following is/are amphotetic?
    (1) BeO (2) Ag_2O
    (3) CO_2 (4) SnO_2

17. Decomposition of oxalic acid in the presence of conc H_2SO_4 gives:
    (1) CO (2) CO_2
    (3) Formic acid (4) H_2O

18. Which of the following is/are true about silicones?
    (1) They are formed by hydrolysis of R_2SiCl_2
    (2) They are polymer, made up of R_2SiO_2 units
    (3) They are made up of SiO_4^{4-} units
    (4) They are macromolecules

19. Which of the following metal oxides are reduced by CO?
    (1) ZnO (2) Fe_2O_3
    (3) CaO (4) Al_2O_3

20. Which of the following species are not known?
    (1) $[SiCl_6]^{2-}$ (2) $[CF_6]^{2-}$
    (3) $[PbCl_6]^{2-}$ (4) $[SiF_6]^{2-}$

21. The incorrect statement(s) among the following is/are:
(1) NCl_5 does not exist but PCl_5 does
(2) Lead prefers to form tetravalent compounds
(3) The three C–O bonds are not equal in the CO_3^{2-} ion.
(4) Both $O_2^{\oplus}$ and NO are paramagnetic.

22. Coal gas
(1) burns with a smoky flame
(2) burns with non-smoky flame
(3) is a good fuel
(4) is not used for lighting purposes

23. Select incorrect statements
(1) Oxalic acid on heating with conc. H_2SO_4 evolves CO gas
(2) In double chain silicate, each Si atom is shared by 2.5 O-atom
(3) $(Si_2O_5)_n^{2-}$ is formula of double chain silicate
(4) SiO_4^{4-} units polymerize to form silicate because Si atom has less tendency to form π-bond with O-atom

24. Select correct statements
(1) Cyclic silicate having 3 Si-atom ($Si_3O_9^{6-}$) contains 6 (Si–O–Si) linkage
(2) $Pb(NO_3)_2$ on strong heating gives PbO_2, O_2 and NO
(3) The stability of dihalides are in the order
$PbX_2 > SnX_2 > GeX_2 > SiX_2 > CX_2$
(4) SiO_2 react with both Na_2CO_3 and HF

25. Select correct statements
(1) PbO can be dissolve in H_2SO_4 or HCl
(2) PbO_2 shows oxidizing properties with HCl and SO_2
(3) Pb_3O_4 reacts with conc. HCl to gives Cl_2 gas
(4) Sn^{2+} and Fe^{3+} cannot co-exit in the same solution.

26. Select correct statements
(1) Silicones are macromolecules formed by hydrolysis of R_2SiCl_2.
(2) Pb pipes are corroded by CH_3COOH
(3) Hydrolysis of $RSiCl_3$ gives cross linked silicones
(4) The structure of mica, asbestos and quartz have the common basic units of SiO_4^{4-}.

Linked Comprehension Type

Paragraph 1

Gaseous fuels due to their advantages over other types of fuels are becoming highly popular. The advantages of the gaseous fuels are as follows:

(1) High calorific value.
(2) Do not produce smoke and do not leave ash after combustion.
(3) They can flow through pipes and can be ignited at a moment's notice at any place. No special devices are required for their combustion.

i. *Coal gas* is a good gaseous fuel as it contains 95% combustible gaseous such as H_2, CH_4, CO etc. It is obtained by destructive distillation of coal at 1000°C.

ii. *Water gas* is a mixture of CO and H_2 and is prepared by passing steam over incandescent coke. The reaction is however endothermic.

iii. *Producer gas*, which possesses low calorific value, is prepared by passing air over red hot coke. It contains mainly nitrogen and CO.

iv. *Semi-water gas* is a mixture of water gas and producer gas.

v. *Oil gas*, which is used in laboratories, is obtained by cracking of kerosene. It is a mixture of hydrocarbon (saturated and unsaturated), mainly lower hydrocarbons.

vi. LPG, which contains C_3 and C_4 hydrocarbon of the alkane and alkene series, supplied in cylinders for domestic uses is very popular these days.

1. Which gas is the essential constituent of most of the fuels?
(1) CO (2) O_2
(3) CO_2 (4) N_2

2. Which fuel has the highest calorific value?
(1) Coal gas (2) Water gas
(3) Producer gas (4) Natural gas

3. Which one is the best fuel in kitchen?
(1) Wood (2) Coal
(3) Kerosene (4) LPG

4. Which one of following fuels has highest percentage of CO?
(1) Coal gas (2) Water gas
(3) Producer gas (4) Natural gas

5. Which one of following is a cracking process?
(1) $C_3H_6 + H_2 \longrightarrow C_3H_8$
(2) $nC_2H_4 \longrightarrow (C_2H_4)_n$
(3) $C_6H_{34} \longrightarrow 6CH_4 + 2C_2H_4 + C_2H_2 + 4C$
(4) $3C_2H_2 \longrightarrow C_6H_6$

6. LPG stands for:
(1) Liquefied petroleum gas
(2) Liquefied producer gas
(3) Laboratory petroleum gas
(4) Laboratory producer gas

7. Producer gas is
(1) $CO + H_2$ (2) $CO + N_2$
(3) $CO + CH_4 + H_2$ (4) $CO + H_2O$

Paragraph 2

On fusion of a mixture of Na_2CO_3 and $CaCO_3$ with silica at 1500°C, a liquid consisting of silicates of sodium and calcium is formed. On cooling, liquid become viscous and eventually ceases to flow. It becomes solid and is known as glass. By varying the proportions of the three basic ingredients and by adding other substances, the properties of glass can be altered. Glass can be represented as $R_2O{\cdot}MO{\cdot}6SiO_2$, where R = Na or K; M = Ca, Ba, Zn or Pb. SiO_2 may be replaced by Al_2O_3, B_2O_3 or P_2O_5. Coloured glasses are obtained by adding certain metallic oxides or salts in the fused mass. Glass is attached by HF and this property is used to make marking on the glass. This is known as etching. The glass

rapid cooling becomes brittle and fragile. The articles of glass are cooled neither slowly nor very rapidly. The process of gradual cooling of glass is called annealing.

8. Glass is
(1) Solid (2) Liquid
(3) Supercooled liquid (4) Colloidal solution

9. Ordinary glass is
(1) Sodium silicate and silica
(2) Calcium silicate and silica
(3) Potassium silicate and silica
(4) Mixture of sodium and calcium silicates with silica.

10. The acid that cannot be stored in glass is
(1) HF (2) HCl
(3) HBr (4) HI

11. Annealing is
(1) Slow and gradual cooling (2) Rapid cooling
(3) Cooling by water (4) Slow cooling

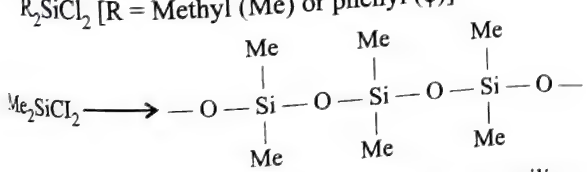
12. A special type of glass which contains cerium oxide and does not allow the passage of ultraviolet rays is called
(1) Flint glass (2) Crooke's glass
(3) Hard glass (4) Pyrex glass

13. Blue colour can be imparted to the glass by
(1) CoO (2) Fe_2O_3
(3) NiO (4) Cu_2O

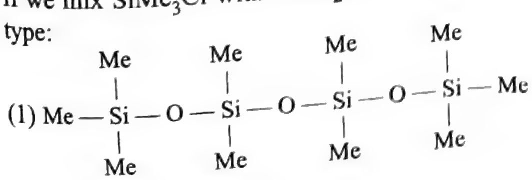
Paragraph 3

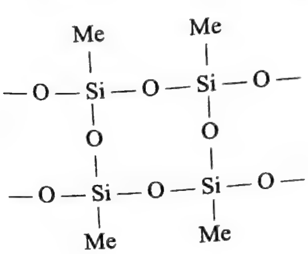
Silicones are synthetic polymers containing repeated R_2SiO units. Since the empirical formula is that of a ketone (R_2CO), the name silicone has been given to these materials. Silicones can be made into oils, rubbery elastomers and resins. They find a variety of applications because of their chemical inertness, water repelling nature, heat resistance and good electrical insulating property. Commercial silicon polymers are usually methyl derivatives and to a lesser extent phenyl derivatives and are synthesised by the hydrolysis of

R_2SiCl_2 [R = Methyl (Me) or phenyl (ϕ)]



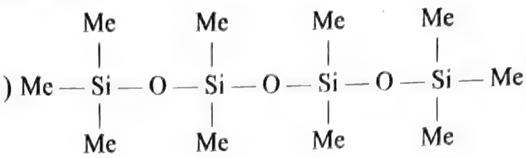
14. If we mix $SiMe_3Cl$ with $SiMe_2Cl_2$, we get silicones of the type:

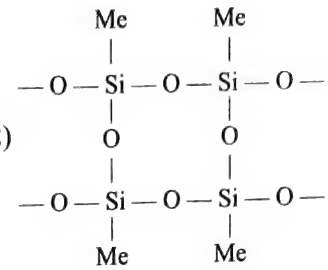
(1) 

(2) 

(3) both of the above
(4) none of the above

15. If we start with $SiMeCl_3$ as the starting material, silicones formed is:

(1) 

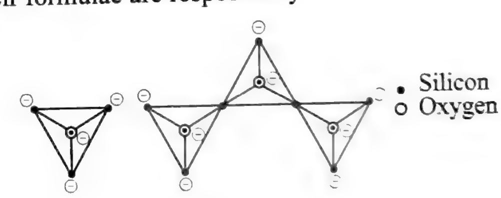
(2) 

(3) Both of the above
(4) None of the above

Paragraph 4

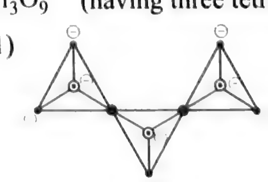
The name 'silica' covers an entire group of minerals which have the general formula SiO_2, the most common of which is quartz. Quartz is a framework silicate with SiO_4 tetrahedra arranged in spirals. *The spirals can turn in a clockwise or anti-clockwise direction—a feature that results in there being two mirror images, optically active, varieties of quartz.*

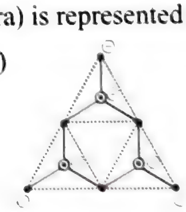
16. The following pictures represent various silicate anions. Their formulae are respectively:



(1) SiO_3^{2-} $Si_3O_7^{2-}$
(2) SiO_4^{4-} $Si_3O_{10}^{8-}$
(3) SiO_4^{2-} $Si_3O_9^{2-}$
(4) SiO_3^{4-} $Si_3O_7^{8-}$

17. $Si_3O_9^{6-}$ (having three tetrahedra) is represented as:

(1) 

(2) 

(3) both (4) none

18. The silicate anion in the mineral kinoite is a chain of three SiO_4^{4-} tetrahedra that share corners with the adjacent tatrahedra. The mineral also contains Ca^{2+} ions, Cu^{2+} ions and water molecules in a 1 : 1 : 1 ratio. This mineral is represented as:
(1) $CaCuSi_3O_{10}{\cdot}H_2O$ (2) $CaCuSi_3O_{10}{\cdot}2H_2O$
(3) $Ca_2Cu_2Si_3O_{10}{\cdot}2H_2O$ (4) none of these

Paragraph 5

In some foam-type fire extinguishers, the reactants are $Al_2(SO_4)_3$ (aq) and $NaHCO_3$ (aq). When the extinguisher is activated, these reactants are allowed to mix producing $Al(OH)_{3(s)}$ and $CO_{2(g)}$. The $Al(OH)_3 - CO_2$ foam extinguishes the fire.

19. CO_2 is formed as a result of :

(1) reaction between Al^{3+} and $HCO_3^{\ominus}$

(2) reaction between hydrolysis product of Al^{3+} and $HCO_3^{\ominus}$

(3) reaction between hydrolysis product of $NaHCO_3$ and $Al_2(SO_4)_3$

(4) direct reaction between $Al_2(SO_4)_3$ and $NaHCO_3$

20. Net ionic reaction of the above chemical change is:

(1) $Al^{3+} + HCO_3^{\ominus} + H_2O \longrightarrow Al(OH)_3 + CO_2$

(2) $Al^{3+} + HCO_3^{\ominus} + \overset{\ominus}{O}H \longrightarrow Al(OH)_3 + CO_2 + H_2O$

(3) $[Al(H_2O)_6]^{3+}\ HCO_3^{\ominus} \longrightarrow Al(OH)_3 + CO_2 + H_2O$

(4) $Al_2(SO_4)_3 + NaHCO_3 \longrightarrow Na_2SO_4 + Al(OH)_3 + H_2O$

21. Addition of Na_2CO_3 to a solution of an oxide in water produces CO_2. This experiment indicates that:

(1) the oxide is that of a non-metal

(2) the oxide is basic

(3) the oxide is amphoteric

(4) the oxide is neutral

Paragraph 6

CO_2 and H_2O absorbs strongly in the infrared region, and its presence in the atmosphere decreases the loss of heat from the earth by radiation. This global warming is called the 'greenhouse effect' (other gases, including the oxides of nitrogen from car exhausts, freons from aerosols and refrigerators and methane from bacteria in the soil and in the rumen of cows, also add to the greenhouse effect). The concentration of atmospheric CO_2 has increased by 10%. This is resulting in the increase in the mean temperature of the earth by 2.5°C, varying from 2°C at the equator to 4°C at the poles. This could have dramatic effects on the climate.

22. As a result of greenhouse effect, there can be:

A: an increase in rate of evaporation of water, thus, untimely more rain, flooding etc.

B: tropical storms in certain parts of the world

C: a decrease in pH of the soil

D: an increase in pH of the soil

Select correct alternate :

(1) B, C, D (2) A, C, D

(3) A, B, D (4) A, B, C

23. Which of the following is growing at a faster rate than CO_2 and thus responsible for the greenhouse effect?

(1) CFC (2) N_2O

(3) O_3 (4) CH_4

24. Instead of monitoring carbon dioxide, suggest another gas that scientists could study to substantiate the fact that CO_2 concentration is steadily increasing in the atmosphere?

(1) N_2O (2) O_2

(3) CH_4 (4) O_3

25. The equilibrium constant (K_p) for the reaction

$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$

is 1.4×10^{90} at 25°C. Given this enormous value, why does not CO convert totally into CO_2 in the troposphere?

(1) CO forms complex with haemoglobin

(2) CO has low solubility in H_2O

(3) CO has high activation energy

(4) CO is toxic in nature

Paragraph 7

In the first biological application of bucky ball, chemists at the University of California at San Francisco and Santa Barbara made a discovery in 1993 that could help in designing drugs to treat AIDS. The human immunodeficiency virus (HIV) that causes AIDS reproduces by synthesising a long protein chain, which is cut into smaller segments by an enzyme called HIV-protease. One way to stop AIDS, then might be to inactivate the enzyme. When the chemists reacted a water-soluble derivative of bucky ball with HIV-protease, they found that it binds to the portion of the enzyme that would ordinarily cleave the reproductive protein, thereby preventing the HIV virus from reproducing. Consequently, the virus could no longer infect the human cells they had grown in the laboratory. The bucky ball compound itself is not a suitable drug for use against AIDS because of potential side effects and delivery difficulties, but it does provide a model for the development of such drugs.

26. Bucky ball is the allotrope of:

(1) phosphorus (2) sulphur

(3) carbon (4) titanium

27. What is the formula of the bucky ball?

(1) P_4 (2) S_8

(3) Ti_3 (4) C_{60}

28. In bucky ball each atom is:

(1) sp^2-hybridised element with extensive delocalised molecular orbital.

(2) sp^2-hybridised element with localised molecular orbital.

(3) sp^3-hybridised element with delocalised molecular orbital.

(4) sp^3-hybridised element with localised molecular orbital.

29. Consider following statements about bucky ball:

A : It is also called fullerene

B : It is also called Buckministerfullerene

C : Bucky tubes (made of fullerenes) are several times stronger than steel wires

D : Bucky ball is a plastic polymer

Select correct statement (s) :

(1) A, C, D (2) A, B, C

(3) A, B, D (4) B, C, D

Paragraph 8

Elemental carbon appears in many structural forms or allotropes. Three of these forms are crystalline—diamond, graphite and the recently discovered fullerene (bucky ball)—while more than 40 others including coke and carbon black are amorphous. Now there

...to be set a fourth crystalline allotrope of carbon, reported in ...by Rich and Lagow at the University of Texas.

...Newly discovered allotrope of carbon has the form:

(1) polyyne (2) fullerene
(3) bucky ball (4) none of these

... Structures of different allotropes of carbon have been compared. Which represents incorrect comparison?

(1) allotrope discovered in 1995 — sp-hybridised carbon
(2) bucky ball — sp-hybridised carbon
(3) graphite — sp^2-hybridised carbon
(4) diamond — sp^3-hybridised carbon

Matrix Match Type

This section contains question each with two columns I and II. Match the items in column I with that in the column II.

1.

	Column I		Column II
a.	Lead acetate	i.	Carborundum
b.	$SnCl_4 \cdot 5H_2O$	ii.	Hydrides of silicon
c.	$SnCl_2$	iii.	Butter of tin
d.	SiC	iv.	Sugar of lead
e.	PbO_2	v.	Oxidising agent
f.	Silanes	vi.	Reducing agent

2.

	Column I		Column II
a.	Shows $p\pi-p\pi$ back bonding	i.	Graphite
b.	Shows $p\pi-d\pi$ back bonding	ii.	BCl_3
c.	Lewis acid	iii.	$N(SiH_3)_3$
d.	Shows inert pair effect	iv.	BF_3
e.	Greenhouse gas	v.	Gallium
f.	Lead pencil	vi.	CO_2

3.

	Column I		Column II
a.	Boron + NaOH	i.	Si – O – Si linkages
b.	$(B_4O_7)^{2-} \longrightarrow [B(OH)_3]$	ii.	Na_3BO_3 and H_2
c.	$B_2H_6 \longrightarrow H_3BO_3$	iii.	Acidification
d.	$B_2H_6 \longrightarrow$ Borazine	iv.	High temperature and pressure
e.	Silicones	vi.	Ammonolysis
f.	Graphite $\longrightarrow$ Diamond	v.	Hydrolysis

4.

	Column I		Column II
a.	$(SiH_3)_3N$	i.	Reducing agent
b.	$(CH_3)_3N$	ii.	$p\pi-d\pi$ overlap between Si and N
c.	$B(OH)_3$	iii.	Triangular, BO_3^{3-} units
d.	$Ti(NO_3)_3$	iv.	Lewis base
e.	$SnCl_2$	v.	No donor property
f.	CCl_4	vi.	Oxidising agent

5.

	Column I		Column II
a.	Galena	i.	$PbCrO_4$
b.	Cerussite	ii.	$PbO \cdot PbSO_4$
c.	Anglesite	iii.	PbS
d.	Lanarkite	iv.	$PbCO_3$
e.	Yellow pigment	v.	PbO
f.	Massicot or litharge	vi.	$PbSO_4$

6.

	Column I		Column II
a.	Sublimed white lead	i.	$Pb(CH_3COO)_2$
b.	Chrome red	ii.	Pb_2O
c.	Sugar of lead	iii.	$Pb(OH)_2 \cdot PbCrO_4$
d.	Lead lotion	iv.	Solution of basic lead acetate
e.	Lead suboxide	v.	Pb_2O_5
f.	Lead sesquioxide	vi.	$PbSO_4 + PbO + ZnO$

7.

	Column I (Characteristics of silicates)		Column II (Silicates)
a.	Three shared corners and ten unshared corners	i.	$(Si_4O_{13})^{10-}$
b.	Negative charge on the anion is equal to the number of terminal O-atoms	ii.	$(SiO_4)^{4-}$
c.	Non-planar geometry	iii.	$(Si_4O_{12})^{8-}$
d.	Si atom(s) is/are present at the center of geometry and every O-atom is present at each corner of geometry	iv.	$(Si_2O_7)^{6-}$

8.

	Column I		Column II
a.	Sheet silicate	i.	3-corner O-atom are bonded
b.	Pyrosilicate	ii.	Non-planar
c.	Pyroxene chain	iii.	$(Si_4O_{11})_n^{6n-}$
d.	Amphibole chain	iv.	$(SiO_3)_n^{2n-}$

9. Match the items given in Column I with that in Column II and III.

Column I		Column II		Column III	
a.	Fullerenes (resembles a Soccer ball)	i.	C_{70}	p.	$C + H_2O(g) \xrightarrow{473-1273K} CO(g) + H_2(g)$
b.	Fullerenes (resembles a Rugby ball)	ii.	C_{60}	q.	12-Five membered rings 20-six membered rings
c.	Producer gas	iii.	Industrial fuels	r.	12-Five membered rings 25-six membered rings
d.	Water gas	iv.	Synthesis gas	s.	$2C + O_2(g) + 4N_2(g) \xrightarrow{1273\ K} 2CO(g) + 4N_2(g)$

For Q.10 to Q.14

Answer the questions given below by appropriately matching the information given in three column of the following table.

Column I		Column II		Column III	
	E.C. of 14 Group Elements		Characteristics (I)		Characteristics (II)
a.	$6s^2, 6p^2$	i.	Carborundum is hard and refractory material which is used as an abrasive	p.	Used in IR prisms and lenses
b.	$5s^2, 5p^2$	ii.	Metalloid	q.	Lovest ionisation enthalpy
c.	$4s^2, 4p^2$	iii.	More Stable in (+2) oxidation state	r.	Tendency to form ($p\pi$-$p\pi$)multiple bonds
d.	$3s^2, 3p^2$	iv.	Do not show inert pair effect	s.	Non-metals
e.	$2s^2, 2p^2$	v.	Three allotropes. Grey, White (most stable) and Rhombic		Soft metals with low melting points

10. For lead, correct combination is:
(1) b–v–q, t (2) a–iii–t
(3) b–v–q (4) b–v–t

11. For carbon, correct combination is:
(1) d–i, iv–s (2) d–i–s
(3) e–iv–s (4) e–iv–s, r

12. For germanium, correct combination is:
(1) c–ii–p (2) b–v–q, t
(3) b–v–q (4) b–v–t

13. For silicon, correct combination is:
(1) d–i–s (2) d–iv–s
(3) d–i, iv–s (4) c–ii–p

14. For tin, correct combination is:
(1) c–ii–p (2) b–v–q, t
(3) b–v–q (4) a–iii–t

Numerical Value Type

1. Carbogen is a mixture of O_2 and CO_2. It is used for artificial respiration. What is the percentage of CO_2 in this mixture?
2. What is the bond order of carbon monoxide?
3. In the structure of silica, each silicon atom is bonded to how many oxygen atoms?
4. Pb_3O_4 is regarded as a compound oxide of PbO and PbO_2. How many parts of PbO_2 are present in it?
5. How many moles of methane are obtained by the hydrolysis of one mole of aluminium carbide?
6. How many moles of $PbCO_3$ are present in white lead?
7. What is the percentage of lead in lead pencil?

Archives

JEE ADVANCED

Single Correct Answer Type

1. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are
(1) CH_3SiCl_3 and $Si(CH_3)_4$
(2) $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$
(3) $(CH_3)_2SiCl_2$ and CH_3SiCl_3
(4) $SiCl_4$ and $(CH_3)_3SiCl$
(JEE Advanced 2015)

Multiple Correct Answers Type

1. With respect to graphite and diamond, which of the following statement(s) given below is(are) correct?
(1) Graphite is harder than diamond.
(2) Graphite has higher electrical conductivity than diamond.
(3) Graphite has higher thermal conductivity than diamond.
(4) Graphite has higher C–C bond order than diamond.
(IIT-JEE 2012)

Answers Key

EXERCISES

Single Correct Answer Type

1. (2)	**2.** (3)	**3.** (4)	**4.** (2)	**5.** (4)
6. (2)	**7.** (2)	**8.** (4)	**9.** (2)	**10.** (1)
11. (4)	**12.** (2)	**13.** (4)	**14.** (3)	**15.** (3)
16. (2)	**17.** (1)	**18.** (3)	**19.** (1)	**20.** (1)
21. (4)	**22.** (3)	**23.** (2)	**24.** (1)	**25.** (2)
26. (1)	**27.** (1)	**28.** (1)	**29.** (1)	**30.** (4)
31. (4)	**32.** (1)	**33.** (4)	**34.** (3)	**35.** (4)
36. (3)	**37.** (4)	**38.** (4)	**39.** (3)	**40.** (4)
41. (3)	**42.** (2)	**43.** (1)	**44.** (3)	**45.** (4)
46. (3)	**47.** (2)	**48.** (3)	**49.** (2)	**50.** (4)
51. (1)	**52.** (3)	**53.** (4)	**54.** (3)	**55.** (3)
56. (2)	**57.** (4)	**58.** (2)	**59.** (3)	**60.** (2)
61. (1)	**62.** (4)	**63.** (4)	**64.** (4)	**65.** (2)
66. (4)	**67.** (3)	**68.** (1)	**69.** (4)	**70.** (4)
71. (2)	**72.** (4)	**73.** (3)	**74.** (1)	**75.** (2)
76. (2)	**77.** (3)	**78.** (3)	**79.** (3)	**80.** (3)
81. (3)	**82.** (3)	**83.** (1)	**84.** (2)	**85.** (2)
86. (2)	**87.** (2)	**88.** (1)	**89.** (4)	**90.** (4)
91. (3)	**92.** (2)	**93.** (3)	**94.** (1)	**95.** (4)
96. (2)	**97.** (1)	**98.** (1)	**99.** (2)	**100.** (4)
101. (2)	**102.** (1)	**103.** (1)	**104.** (1)	**105.** (4)
106. (4)	**107.** (4)	**108.** (3)	**109.** (2)	**110.** (4)
111. (4)				

Multiple Correct Answers Type

1. (2, 4)	**2.** (1, 2, 4)	**3.** (1, 3, 4)
4. (1, 2)	**5.** (3, 4)	**6.** (2, 4)
7. (1, 2, 3, 4)	**8.** (1, 2, 4)	**9.** (1, 2, 3)
10. (2, 3)	**11.** (1, 4)	**12.** (2, 3)
13. (2, 3)	**14.** (1, 3)	**15.** (2, 3)
16. (1, 4)	**17.** (1, 2, 4)	**18.** (1, 2, 4)
19. (1, 2)	**20.** (2, 4)	**21.** (2, 3)
22. (2, 3)	**23.** (1, 3)	**24.** (3, 4)
25. (2, 3, 4)	**26.** (1, 2, 3, 4)	

Linked Comprehension Type

1. (1)	**2.** (1)	**3.** (4)	**4.** (2)	**5.** (3)
6. (1)	**7.** (2)	**8.** (3)	**9.** (4)	**10.** (1)
11. (1)	**12.** (3)	**13.** (1)	**14.** (1)	**15.** (2)
16. (2)	**17.** (2)	**18.** (3)	**19.** (2)	**20.** (3)
21. (1)	**22.** (4)	**23.** (1)	**24.** (2)	**25.** (3)
26. (3)	**27.** (4)	**28.** (1)	**29.** (2)	**30.** (1)
31. (2)				

Matrix Match Type

Q. No.	a	b	c	d	e	f
1.	iv	iii	vi	i	v	ii
2.	ii, iv	iii	ii, iv	v	vi	i
3.	ii, iii	iii	v	vi	i	iv
4.	ii, v	iv	iii	vi	i	v
5.	iii	iv	vi	ii	i	v
6.	iv	iii	i	iv	ii	v

7. (a → i; b → i, ii, iii, iv; c → i, ii, iii, iv; d → i, ii, iii, iv)
8. (a → i, ii; b → iv; c → ii, iv; d → ii, iii, iv)
9. (a → ii-q; b → i-r; c → iii-s; d → iii, iv-p)

10. (2)	**11.** (4)	**12.** (1)	**13.** (3)	**14.** (2)

Numerical Value Type

1. (5)	**2.** (3)	**3.** (4)	**4.** (1)	**5.** (3)
6. (2)	**7.** (0)			

ARCHIVES

JEE Advanced

Single Correct Answer Type

1. (2)

Multiple Correct Answers Type

1. (2, 4)